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THE

PHYSICAL REVIEW

SOME RELATIONSHIPS BETWEEN SINGLETS AND TRIPLETS IN THE SPECTRA OF TWO ELECTRON SYSTEMS

By William V. Houston

Abstract

The Darwin-Pauli treatment of the electron is applied to the Schroedinger equation for a two electron system. The results show that the division into singlets and triplets is justified only as a limiting case. Expressions are derived which give the position of the levels, the Zeeman effect pattern, and the intensities of the lines when the division into singlet and triplet cannot strictly be made. These expressions are shown to give the observed facts of several spectra.

THE work of Heisenberg[1] on resonance in quantum mechanics has made it possible, in principle, to calculate the spectrum of any complex atom. The difficulties involved are the purely mathematical ones of finding the solutions of the Schroedinger equation. There will be given here some results which show the amount of information which can be secured from a simple perturbation calculation.

The problem treated is that of two electrons in an arbitrary central field, with the restriction that one electron is in an *s* orbit. By the use of the Darwin-Pauli[2] treatment of the "spinning electron" it is possible to determine the energy levels with and without a magnetic field, in the first approximation. The levels without the field show to what extent a division into a singlet and a triplet system is justified, while the levels with the field show the deviations from the Landé *g*-formula which are to be expected. The calculated transition probabilities then show that the observed intensity of the intercombination lines is usually due to the metastability of the upper level.

1. *The Schroedinger equation.* The characteristic functions of the problem will be functions of four independent variables for each electron. There are the three space coordinates of the electron and the "spin" variable. These functions, in the zero approximation, may be written in the usual way as products of four functions of one variable only. The function of the coordinates is $R_{ln}P_l^m$, where R is a function of the radius only, and P is a spherical harmonic defined by

[1] W. Heisenberg, Zeits. f. Physik **38**, 411 (1926).

[2] Pauli, Zeits. f. Physik **43**, 624 (1927); Darwin, Proc. Roy. Soc. **A116**, 227 (1927).

$$P_l^m = (l-m)!\sin^m\theta\left(\frac{d}{d\cos\theta}\right)^{l+m}\frac{(-\sin^2\theta)^l}{2^l l!}e^{im\phi} \tag{1}$$

n, l, and m are the quantum integers and satisfy the conditions $l<n$, $-l\leqq m\leqq l$. The function S of the spin variable is peculiar in that the variable itself is discontinuous and can take only two values which we may designate by subscripts S_α and S_β. The function $|S_\alpha|^2$ represents the probability that the moment of the electron is parallel to the field, while $|S_\beta|^2$ represents the probability that the electron is pointing in the opposite direction. The normalization is given by

$$|S_\alpha|^2+|S_\beta|^2=1 \tag{2}$$

In a strong magnetic field, with a given energy, either S_α or S_β is equal to one and the other is zero. It is this function for a strong magnetic field which is to be used here, since the total function is written as a sum of products of the independent coordinate and spin functions.

The Hamiltonian function as an operator may be written in three parts so that

$$H\psi=H^0\psi+H'\psi+H''\psi=E\psi \tag{3}$$

where H^0 includes the ordinary kinetic and potential energy with relativity, in the central field. H' is the electrostatic interaction of the two electrons, i.e.,

$$H'=e^2/r_{12} \tag{4}$$

while

$$H''=\frac{h^2}{16\pi^2}\frac{Ze^2}{m_0^2c^2}\frac{1}{i}\sum_{j=1,2}\frac{1}{rj^3}(k\cdot s)_j+\mu\sum_{j=1,2}\{(\mathfrak{K}\cdot s)_j-(\mathfrak{K}\cdot k)_j\} \tag{5}$$

The subscripts $_1$ and $_2$ indicate that the operation is to be carried out on the coordinates of the first or second electron only. The components of k are

$$k_x=y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y};\qquad k_y=z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z};\qquad k_z=x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x} \tag{6}$$

and

$$\mu=\frac{eh}{4\pi m_0 c}.$$

s is a vector operator which operates on S only and is defined by the relations

$$\begin{aligned} s_xS_\alpha&=S_\beta & s_xS_\beta&=S_\alpha\\ s_yS_\alpha&=iS_\beta & s_yS_\beta&=-iS_\alpha\\ s_zS_\alpha&=S_\alpha & s_zS_\beta&=-S_\beta. \end{aligned} \tag{7}$$

This Hamiltonian neglects the magnetic interaction between the two electrons and between each electron and the orbit of the other. These, however, are quantities of the order $1/Z$ compared with H'', so that for ele-

ments of high atomic number their effect should be small. The Z here is not, of course, the true atomic number, but is the atomic number which is effective for the multiplet separation.

2. *The secular equation.* The results of the perturbation H' are known from Heisenberg's[1] work on helium. The characteristic functions of the space coordinates divide into two groups, symmetric and antisymmetric in the two electrons. The energy levels corresponding to these two groups differ by

$$\gamma X = \int H' R_{0n'} P_0^0(1) R_{ln} P_l^m(2) R_{0n'} P_0^0(2) R_{ln} P_l^m(1) d\tau \tag{8}$$

where we define γ by

$$\gamma = \frac{h^2}{16\pi^2} \frac{Ze^2}{m_0^2 c^2} \int R_{ln}^2 \frac{1}{r^3} d\tau$$

With each of these functions may be combined the four possible spin functions. Of the eight groups of functions which result, only the four which are antisymmetric in the two electrons are permitted. Because of this known effect of the perturbation H', it is convenient to take as the functions of the unperturbed system the four functions:

$$\begin{aligned}
\phi_1 &= (1/2)\{P_0^0(1)P_l^m(2)+P_0^0(2)P_l^m(1)\}\{S_\alpha(1)S_\beta(2)-S_\beta(1)S_\alpha(2)\}\\
\phi_2 &= (1/2^{1/2})\{P_0^0(1)P_l^{m-1}(2)-P_0^0(2)P_l^{m-1}(1)\}S_\alpha(1)S_\alpha(2)\\
\phi_3 &= (1/2)\{P_0^0(1)P_l^m(2)-P_0^0(2)P_l^m(1)\}\{S_\alpha(1)S_\beta(2)+S_\beta(1)S_\alpha(2)\}\\
\phi_4 &= (1/2^{1/2})\{P_0^0(1)P_l^{m+1}(2)-P_0^0(2)P_l^{m+1}(1)\}S_\beta(1)S_\beta(2).
\end{aligned} \tag{9}$$

The radial function which is common to all four is not written. The zero approximation for the perturbed system is given by a linear combination of these four

$$\psi = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + a_4\phi_4 \tag{10}$$

The secular equation may then be written as the determinant[3]

$$\begin{vmatrix}
X+\omega m-\epsilon & 1 & -m & 1 \\
1 & 2\dfrac{\omega(m+1)+m-1-\epsilon}{(l+m)(l-m+1)} & 1 & 0 \\
-m & 1 & \omega m-\epsilon & -1 \\
1 & 0 & -1 & 2\dfrac{\omega(m-1)-m-1-\epsilon}{(l-m)(l+m+1)}
\end{vmatrix} = 0 \tag{11}$$

[3] This determinant is not in its original form. The original form may be obtained by multiplying the second row and second column by $-(1/2^{1/2})(l+m)^{1/2}(l-m+1)^{1/2}$ and the fourth row and fourth column by $(1/2^{1/2})\,(l-m)^{1/2}(l+m+1)^{1/2}$.

where $\omega=\mu/\gamma$ and $\gamma\epsilon=\Delta E$. This really represents a selection of four functions out of all those having the same energy on account of the degeneracy in m. However if the secular equation is written for all the functions with the same value of l, the determinant can be divided into a number of determinants such as (11).

When ω^2 and higher powers are neglected the roots of this equation are

$$\epsilon_1=\frac{1}{2}(X-1)+\frac{1}{2}\{(X+1)^2+4l^2+4l\}^{1/2}+\omega m\left\{1+\frac{[(X+1)^2+4l^2+4l]^{1/2}-X-1}{2(l^2+l)[(X+1)^2+4l^2+4l]^{1/2}}\right\}$$

$$\epsilon_2=l+\omega m\frac{l+2}{l+1} \tag{12}$$

$$\epsilon_3=\frac{1}{2}(X-1)-\frac{1}{2}\{(X+1)^2+4l^2+4l\}^{1/2}+\omega m\left\{1+\frac{[(X+1)^2+4l^2+4l]^{1/2}+X+1}{2(l^2+l)[(X+1)^2+4l^2+4l]^{1/2}}\right\}$$

$$\epsilon_4=-l-1+\omega m\frac{l-1}{l}\,.$$

3. *The interval rule.* The roots in (12) give the interval rule for triplets, for when $|X|\gg l$ and $\omega=0$

$$\epsilon_1=X\,;\quad \epsilon_2=l\,;\quad \epsilon_3=-1\,;\quad \epsilon_4=-l-1 \tag{13}$$

so that the last three form the triplet with the interval ratio $(l+1)/l$. However, when X is not so large the interval ratio is different and is a function of X. The singlet level, ϵ_1 and the center triplet level, ϵ_3 which has the same inner quantum number, are given by

$$\epsilon_{1,3}=\tfrac{1}{2}(X-1)\pm\tfrac{1}{2}\{(X+1)^2+4l^2+4l\}^{1/2} \tag{14}$$

Thus as X decreases the center triplet level ϵ_3 moves downward; for $X=0$, ϵ_1 and ϵ_3 coincide with the two outer triplet levels ϵ_2 and ϵ_4; while for $X\to-\infty$, ϵ_1 has become the center triplet level and ϵ_3 is the singlet level. Thus the division into singlet and triplet has a meaning only when $|X|\gg l$.[4]

Because of the terms neglected in the Hamiltonian function, and because this is only the first approximation for the terms considered, it cannot be expected that Eq. (12) will exactly represent the observations. Table I shows, however, that in a number of representative cases the observations are pretty well given. In this table are given the values of the singlet and triplet terms measured from a zero between the two outer triplet terms. This zero is determined from the values of ϵ_2 and ϵ_4 in Eq. (13). From the values of the two outer triplet levels and the singlet level the third triplet level is determined from the two relations:

$$(\epsilon_1+1)(\epsilon_3+1)=-(l^2+l) \tag{15}$$

$$\epsilon_2-\epsilon_4=2l+1 \tag{16}$$

[4] Dingle, Proc. Roy. Soc. A100, 167 (1922), recognized this in treating mercury as a quartette system.

The last column gives the position of the inner triplet level determined from the usual interval rule.

TABLE I.

Terms			$\gamma\epsilon_1$	$\gamma\epsilon_2$	$\gamma\epsilon_4$	$\gamma\epsilon_3$ obs.	$\gamma\epsilon_3$ calc.	$\gamma\epsilon_3$ norm.
N	II	P	167	56	− 112	− 80	− 84	− 56
N	II	P	1204	57	− 114	− 62	− 62	− 57
N	II	P	500	58	− 115	− 68	− 70	− 58
O	III	P	5447	125	− 250	− 132	− 130	− 125
Si	I	P	1127	91	− 181	− 104	− 105	− 91
Ge	I	P	1425	522	−1044	− 894	− 801	− 522
Sn	I	P	1957	1329	−2658	−2385	−2405	−1329
Pb	I	P	4119	3494	−6988	−6662	−6708	−3494
Cd		$1P$	12435	571	−1142	− 600	− 621	− 571
Cd		$2P$	1597	82	− 163	− 92	− 90	− 82
Cd		$1D$	−275	12	− 18	− 6	− 5	− 6
Cd		$2D$	−228	6	− 9	− 2	− 3	− 3
Hg		$1P$	12158	2133	−4266	−2498	−2769	−2133
Hg		$2P$	649	564	−1127	− 979	−1088	− 564
Hg		$1D$	−60	38	− 57	3	34	− 19
Hg		$2D$	−47	18	− 27	− 4	4	− 9
Hg		$3D$	−32	10	− 15	− 3	5	− 5

In the D terms of Cd and Hg the singlet level is below the triplet level. The agreement for these terms in Hg is not very good but the results are qualitatively correct. A more exact treatment of these levels could be given by considering the whole Hamiltonian function, but the part treated here is enough to show the nature of the connection between the singlet and triplet systems.

4. *The Zeeman effect.* The connection between the singlets and triplets is also shown by the Zeeman effect. Eq. (12) shows that when X is large the Landé g-factor[5] gives the separation of the levels in a weak magnetic field. But as X decreases and passes through zero to a large negative value, the singlet level becomes the center triplet level not only with respect to its position, but also with regard to its Zeeman effect. The two outer triplet levels are independent of X with regard to the Zeeman effect as well as with regard to position.

TABLE II

Term	g observed	g from Eq. (12)	g normal
Sn $^1P_1$	1.125	1.123	1.000
Sn $^3P_1$	1.375	1.377	1.500
Pb $^1P_1$	1.150	1.148	1.000
Pb $^3P_1$	1.350	1.352	1.500

Table II gives the observed and calculated g values for tin and lead. The agreement in these cases is very satisfactory. Exact measurements on Cd and Hg do not seem to be available.[6]

[5] A. Landé, Zeits. f. Physik **15**, 189 (1923).

[6] The observed values are taken from a paper by Goudsmit and Back, Zeits. f. Physik **40**, 530 (1927) in which the limiting cases X large and $X=0$ are discussed.

According to the Landé formula the sum of the g factors of the three members of a triplet is equal to three, and hence if the singlet term is included the sum of the four values is equal to four. Eq. (12) shows that this sum rule is true only when the singlet is included.

5. *Intensities.* After the roots of Eq. (12) are known it is possible to determine the coefficients a_1, a_2, a_3, and a_4. These may be written

$$a_1=\frac{(m-\epsilon)(m+1+\epsilon)+(l-m)(l+m+1)}{(X+m-\epsilon)(m+1+\epsilon)+(l-m)(l+m+1)}a_3$$

$$a_2=\frac{1}{(2^{1/2})}\frac{(l+m)^{1/2}(l-m+1)^{1/2}}{(m-1-\epsilon)}\frac{\{(X+2m-2\epsilon)(m+1+\epsilon)+2(l-m)(l+m+1)\}}{\{(X+m-\epsilon)(m+1+\epsilon)+(l-m)(l+m+1)\}}a_3 \tag{17}$$

$$a_4=-\frac{1}{(2^{1/2})}\frac{(l-m)^{1/2}(l+m+1)^{1/2}X}{\{(X+m-\epsilon)(m+1+\epsilon)+(l-m)(l+m+1)\}}a_3$$

a_3 is determined from the normalizing relation

$$a_1^2+a_2^2+a_3^2+a_4^2=1.$$

These are for the case $\omega=0$, so they hold for weak fields only.

Table III gives the values of the squares of the amplitudes of the oscillators which represent the transitions. It is simpler to express them in terms of ϵ_1 than in terms of X although this assumes that ϵ_1 is exactly given by Eq. (12). The intensities may be obtained by multiplying by the fourth power of the frequency. The sum rules are seen to hold for all values of X provided the singlet and triplet are considered as forming one system[7] but they hold for these squared amplitudes rather than for the intensities or the transition probabilities.

Here again it is only the two levels with the same inner quantum number which are affected and jumps between the other levels are unaffected. The amplitude squared for the intercombinations between singlets and triplets is roughly inversely proportional to the square of the separation between singlet and triplet systems.[8] The observed intensity of the resonance line in helium and in the alkaline earths is much greater than this.[9] This is due to the fact that the upper level in these cases is metastable except for this transition which has a low probability. The accumulation of atoms in this partly metastable state then makes up for the low transition probability and the line appears with some intensity. This intensity in emission should then decrease with an increase in pressure.

[7] Kronig, Zeits. f. Physik **33**, 261 (1925) expected the sum rules to include both systems. Ornstein and Burger, Zeits. f. Physik **40**, 403 (1926) showed this experimentally for mercury. The observed values in Table IV are from this work.

[8] See also W. Pauli, Handbuch der Physik, XXIII.

[9] The observations of W. Prokofjew, Zeits. f. Physik **50**, 701 (1928) on the transition probabilities as determined from the anomalous dispersion are in good agreement with the predictions of Table III.

TABLE III

$L=L$ / $L=L-1$	ϵ_1 ^1L_l	ϵ_1 $^3L_{l-1}$	ϵ_1 ^3L_l	ϵ_2 $^3L_{l+1}$	Sum
ϵ'_1 $^3(L-1)_l$	$\frac{(2l+1)(2l-1)(l+1)}{(\epsilon_1+1)^2+l^2+l}$	$\frac{1}{l}$	$\frac{(2l+1)(2l-1)(\epsilon_1+1)^2}{l\{(\epsilon_1+1)^2+l^2+l\}}$	$(2l+3)(2l-1)l$	$(2l+1)(2l+1)l$
ϵ'_1 $^3(L-1)_{l-1}$	$\frac{\{(2l+1)(2l-1)(l-1)\{(\epsilon_1'+1)(l+1)-l(\epsilon_1+1)\}^2}{\{(\epsilon_1+1)^2+l^2+l\}\{(\epsilon_1'+1)^2+l^2-l\}}$	$\frac{(2l+1)(2l-1)(\epsilon_1'+1)^2}{l\{(\epsilon_1'+1)^2+l^2-l\}}$	$\frac{(2l+1)(2l-1)(l^2-1)\{(\epsilon_1+1)(\epsilon_1'+1)+l^2\}^2}{l\{(\epsilon_1+1)^2+l^2+l\}\{(\epsilon_1'+1)^2+l^2-l\}}$		$(2l-1)(2l+1)l$
ϵ'_1 $^3(L-1)_{l-2}$		$(2l+1)(2l-3)l$			$(2l-3)(2l+1)l$
ϵ_1' $^1(L-1)_{l-1}$	$\frac{(2l+1)(2l-1)l\{(\epsilon_1+1)(\epsilon_1'+1)+l^2-1\}^2}{\{(\epsilon_1+1)^2+l^2+l\}\{(\epsilon_1'+1)^2+l^2-l\}}$	$\frac{(2l+1)(2l-1)(l-1)}{(\epsilon_1'+1)^2+l^2-l}$	$\frac{(2l+1)(2l-1)(l+1)\{(\epsilon_1+1)(l-1)-(\epsilon_1'+1)l\}^2}{\{(\epsilon_1+1)^2+l^2+l\}\{\epsilon_1'+1)^2+l^2-l\}}$		$(2l-1)(2l+1)l$
Sum	$(2l+1)(2l-1)l$	$(2l-1)(2l-1)l$	$(2l+1)(2l-1)l$	$(2l+3)(2l-1)l$	= his same are the sums of the sums

Table IV gives the observed and calculated intensities for a group of mercury lines. This table illustrates the applicability of the expressions in Table III for cases where a division into singlet and triplet is rather arbitrary. The intensities in the second column are calculated for a large separation between singlet and triplets, while those in the fourth column are calculated by Table III.

TABLE IV.

Hg line	Int. ($X\to\infty$)	Int. Obs.	Table III
3650	100	100	100
3655	17.9	10.8	10.8
3663	1.2	7.9	1.2
3663	0.		7.0

The proper value of X to use in the computations of Table IV is a bit uncertain due to the lack of exactness in the fit of Eq. (12). The value used is the mean of those determined from ϵ_1 and ϵ_2.

6. These calculations show the rather surprising amount of information which may be derived from a first approximation calculation with the Darwin-Pauli method of treating the electron. It is hoped soon to extend this to more complex systems and especially to remove the restriction that one electron must be in an s orbit.

This work was largely carried out in the Institute for Theoretical Physics at Leipzig under the direction of Professor Heisenberg to whom I am much indebted for his kind assistance. I am also indebted to the John Simon Guggenheim Memorial Foundation for the opportunity of studying in Leipzig.

NORMAN BRIDGE LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY.
November 15, 1928.

THE MOLECULAR SPECTRUM OF AMMONIA
I. TWO TYPES OF INFRA-RED VIBRATION BANDS

By G. A. Stinchcomb and E. F. Barker.

Abstract

Wave-lengths and interpretation of the NH_3 absorption bands at 3.0 and 1 9μ —The NH_3 absorption bands at 3.0μ and at 1.9μ have been sufficiently resolved by means of gratings to reveal their fine structure, which proves to be of a different character in the two cases. The 3μ band is associated with a vibration of the electric moment parallel to the symmetry axis of the molecule, yielding one zero branch and a simple rotation series. At 1.9μ there is observed a series of almost equally spaced lines showing a remarkable uniformity in intensity so that the envelope is a single broad maximum instead of the usual doublet. The band center cannot be selected by inspection. The vibration which gives rise to this band is normal to the symmetry axis. From the 3μ band the *moment of inertia* of the molecule ($I=2.83\times 10^{-40}$) about a line normal to the symmetry axis may be determined, but this does not yield the distances between atomic nuclei. The 1.9μ band probably corresponds to one of the four fundamental frequencies. Because of its character it cannot be a harmonic nor a combination of vibrations along the axis as had previously been supposed. The 10μ and the 6μ bands probably correspond to two other fundamentals, but the selection of the fourth fundamental, and the characterization of combination bands must await further analysis to determine the nature of the vibrations involved.

THE infra-red spectrum of ammonia vapor in the region from 1μ to 15μ has been studied by Coblentz[1], Schierkolk[2] and Robertson and Fox[3] using the best resolution available with prism spectrometers. They have observed a number of very intense vibration bands, for the most part unresolved. In the one at 6μ a single sharp zero branch was found, while the one at 10μ shows a pair of zero branches almost equally intense and lying close together. A partial resolution of the rotation series for these two bands was also possible. The bands near 1.5μ, 1.9μ, 2.2μ and 3.0μ were observed as single broad peaks with nothing to indicate the character of the vibrations with which they are associated. Spence succeeded, with the help of a grating, in resolving the 3μ band, obtaining a sharp zero branch and a rotation series rather irregularly spaced because of incomplete separation of the lines. We have re-examined this band with somewhat improved resolution, and also studied the one at 1.9μ,[4] using echelette gratings ruled in this laboratory. For the 3μ region two gratings having respectively 4800 and 7200 lines per inch were used, and for the 1.9μ region one having 14400 lines per inch.

[1] Coblentz, Carnegie Inst. Pub. **35**, 179 (1905).

[2] Schierkolk, Zeits f. Physik **29**, 277 (1924).

[3] Robertson and Fox, Proc. Roy. Soc. **A120**, 128 (1928).

[4] This band was the first one of its type to be observed, although since it was reported (Phys. Rev. **29**, 213, 1927; abstract 27) others have been found for a number of different symmetrical molecules.

The fine structure observed is of a different character in the two cases, and definitely assigns these bands to two different sorts of vibration.

The ammonia gas was generated by gently heating a dry mixture of ammonium chloride and calcium hydroxide, both chemically pure. The only impurity to be expected is water vapor, which was removed by passing the gas through a trap cooled to the temperature of melting ice and then through three twelve-inch drying towers. The character of the absorption, as well as the ease with which it could be reproduced, indicate satisfactory purity. A continuous stream of this dried gas was kept flowing slowly through the absorption cell, the pressure within being not more than 1 mm greater than that outside. This gave assurance that the cell was always filled and the gas undiluted through leakage or by chemical reaction.

The absorption system consisted of two separate chambers identical in all respects, the one containing ammonia and the other air which had been thoroughly dried. The ends of both were closed by mica windows cut from the same sheet and placed at an angle of approximately 30° to the light beam. Some interference due to the mica was observed but the maxima

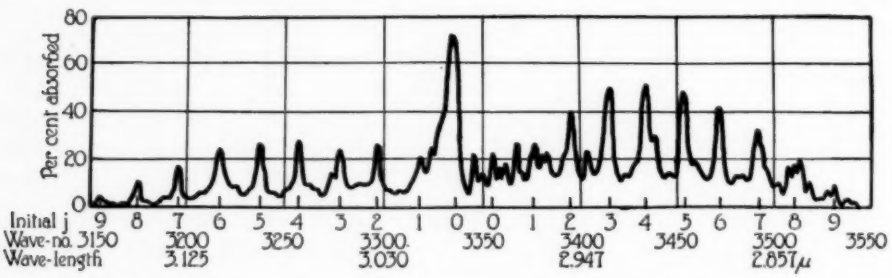

Fig. 1. Absorption pattern for the 3μ band. Vibration of electric moment parallel to symmetry axis. 2 cm cell; slit includes 1.1 wave-numbers.

were far apart and corrections for this effect—never greater than 10 percent of the total absorption—were easily made. The effective cell length was 11.5 cm for most of the observations. In the case of the 3μ band it was found desirable to use a shorter cell also. This required smaller windows so that rock-salt could be conveniently used, and the interference completely avoided.

The absorption pattern for the 3μ band is shown in Fig. 1. It consists of a fairly strong central maximum or zero branch and a rotation series of narrow lines almost equally spaced. These are indicated in the figure by numbers designating the initial rotation states. In addition to these lines there are a number of somewhat weaker ones, and considerable unresolved background, particularly on the high frequency side, suggesting the superposition of other bands of low intensity. Moreover the positive branch (high frequency side) is very much more intense than the negative branch. The observed wave-lengths and frequency differences are shown in Table I. These differences are somewhat smaller in the positive than in the negative branch, and are not as uniform as might be expected. They do not seem to follow a parabolic law as in diatomic molecules. The question of coupling

is here an interesting one which we hope to discuss later. From the spacing of these lines a fairly precise estimate may be made of the moment of inertia of the molecule about an axis normal to the line of symmetry, but this yields no direct information regarding the distances between atomic nuclei. The value is $I = 2.83 \times 10^{-40}$. Bands of this sort are to be expected for symmetrical molecules when the vibration of the electric moment is along the symmetry

TABLE I. *Wave-numbers and wave-number differences in the 3.0μ absorption bands of NH_3.*

Positive branch		Negative branch		Mean	Mean
ν in cm^{-1}	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
3337.0	(center)	—	—	—	—
3355.7	18.7	3318.2	18.8	3337.0	18.75
3377.0	21.3	3296.3	21.9	36.6	20.18
3395.5	18.5	3277.2	19.1	36.3	19.71
3415.3	19.8	3256.8	20.4	36.1	19.81
3433.8	18.5	3236.8	20.0	35.3	19.70
3453.0	19.2	3216.5	20.3	34.8	19.71
3471.6	18.6	3195.8	20.7	33.7	19.70
3490.8	19.2	3175.5	20.3	33.2	19.71
3510.0	19.2	3156.0	19.5	33.0	19.67
				Average	19.67

axis, since the frequency to be associated with any permitted change in rotation is then in first approximation independent of the angle of precession.

The band at 1.9μ, illustrated in Fig. 2, is obviously of a different sort and must arise from a vibration of the electric moment along a line normal to the symmetry axis. Instead of a single band with an intense central absorption peak this yields a whole family of bands whose zero branches

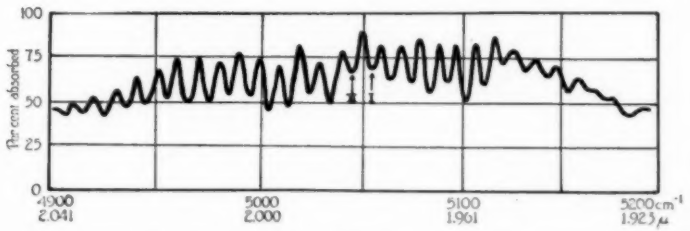

Fig. 2. Absorption pattern for the 1.9μ band. Vibration of electric moment normal to symmetry axis. 11.5 cm cell; slit includes 2.0 wave-numbers.

are separated by an approximately constant frequency difference, in this case about 10 cm^{-1}. There results a characteristic intensity distribution with no well-marked center and with an envelope forming a single maximum instead of the symmetrical doublet so often observed. We have tentatively selected as the central frequency, i.e. the frequency of the vibration from which this band arises, the value 5054 cm^{-1}, marked *I* in the figure, and numbered the lines to the right and left from this point. The reason for adopting this frequency in preference to the value 5045 cm^{-1}, marked *II*,

will be discussed in a subsequent paper. The positions of the lines as observed and the frequency differences between them are shown in Table II.

TABLE II. *Wave-numbers and wave-number differences in the 1.9μ absorption band of NH_3.*

High frequency side				Low frequency side			
ν in cm^{-1}	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
5058.7	8.6	5137.7	11.7	5050.1	9.9	4970.1	10.5
5069.4	10.7	5148.6	10.9	5040.2	11.1	4959.6	9.0
5079.1	9.7	5158.7	10.1	5029.1	9.7	4950.6	10.4
5088.7	9.6	5168.8	10.1	5019.4	10.0	4940.2	9.6
5098.0	9.3	5179.1	10.3	5009.4	9.8	4930.6	10.2
5107.8	9.8			4999.6	9.9	4920.4	9.8
5117.1	9.3			4989.7	9.6	4910.6	10.9
5126.0	8.9			4980.1	10.0	4899.7	—
Mean $\Delta\nu$ 9.98							

Other bands in the ammonia spectrum are now under investigation and will be reported later. It should be emphasized that until the character of the various vibrations appearing in the spectrum of any molecule is known, an attempt to decide which are fundamental and which combination bands is hazardous. Following Schierkolk's measurements which mapped the whole ammonia spectrum Hettner[5] proposed an interpretation of all the strong bands in terms of the two frequencies ν_1 and ν_2, corresponding to 10μ and 6μ, as fundamentals. He believed the bands at 3μ and at 1.9μ to be harmonics, with frequencies $2\nu_2$ and $3\nu_2$ respectively. Hund[6] employed three fundamental frequencies including that of the band at 2.2μ, while Dennison[7] selected four fundamental frequencies, adding that of the 3μ band also. Robertson and Fox[3] have suggested a still different classification. All these writers, however, agree in describing the 1.9μ band, either as an overtone of one or as a combination of two vibrations parallel to the symmetry axis. Our analysis shows conclusively that neither of these possibilities can be correct. We are apparently forced to the conclusion that this is one of the fundamental vibrations. Analysis of the band at 2.2μ, on the other hand, has progressed far enough to suggest that it probably is not. To discuss in detail the mechanical problem of the vibrations in this system will hardly be profitable until the four fundamental frequencies have been definitely determined by observations taken with adequate dispersion.

UNIVERSITY OF MICHIGAN,
DEPARTMENT OF PHYSICS,
December 1, 1928.

[5] Hettner, Zeits. f. Physik **31**, 273 (1925).
[6] Hund, Zeits. f. Physik **31**, 81 (1925).
[7] Dennison, Phil. Mag. **1**, 195 (1926).

THE EFFICIENCY OF QUENCHING COLLISIONS AND THE RADIUS OF THE EXCITED MERCURY ATOM

By E. Gaviola

Abstract

The evidence in favor and against the assumption of Foote that every collision of a foreign gas molecule with an excited mercury atom is efficient in quenching the resonance radiation is discussed, and a new calculation of the efficiency of collisions is given, based on Stuart's measurements, which shows that the efficiency can be assumed to be equal to one in the case of CO, H_2, and perhaps O_2, but that it is undoubtedly smaller than one for H_2O, N_2, A, and He. CO has actually a greater quenching efficiency than H_2. The *radius of the excited mercury atom* is calculated using an improved value for the amount of resonance-radiation re-absorbed in the resonance vessel and found to be $r_{Hg'}=2.91\times10^{-8}$ cm, or 1.62 times larger than the radius of the normal atom for the case of H_2, and $r_{Hg'}=5.5\times10^{-8}$ cm or three-fold normal for the case of CO. The apparent higher quenching efficiency of oxygen than hydrogen is explained by the partial oxidation of the mercury vapor and consequent decrease of the density of the last. It is shown that the *life of metastable atoms* increases with the admission of certain foreign gases into the fluorescence vessel.

Introduction

THE quenching of mercury resonance radiation by foreign gases, first observed by Wood[1] and later studied by Cario,[2] was carefully measured by Stuart[3] in a large range of pressure using several different gases. Stuart found that gases behave in a qualitatively similar manner, in that their effectiveness in quenching the resonance radiation follows a more or less exponential function of the pressure, but that quantitatively they differ widely. Oxygen and hydrogen, for instance, decrease the resonance radiation to one-half its original value at pressures as low as 0.2 mm while with argon and helium it is necessary to approach atmospheric pressure to obtain the same result. Since the number of collisions per second of an excited Hg atom with the molecules of the foreign gases is of the same order of magnitude for all the gases, according to the kinetic theory, Stuart was forced to assume, in order to interpret his experimental results, that the efficiency of the collisions was widely different for the different gases. While every collision of an excited mercury atom with oxygen and nearly every one with hydrogen should be a collision of the second kind, only 1 in 77 would be effective with nitrogen, 1 in 500 with argon, and 1 in 3300 with helium. Furthermore, the number of collisions calculated on the basis of the gas theory, assuming the gas-kinetic collision section for the Hg atom, was not sufficient in the case of oxygen and of hydrogen to explain the observed decrease of 2537, and Stuart made the plausible assumption that the section of the excited atom should

[1] R. W. Wood, Phys. Zeits. **13**, 353 (1912).
[2] G. Cario, Zeits. f. Physik **10**, 185 (1922).
[3] H. Stuart, Zeits. f. Physik **32**, 262 (1925).

be larger than that of the normal atom. Assuming quenching efficiency of oxygen equals 1, he calculated the diameter of the excited mercury to be 3.4 times the diameter of the normal atom. The efficiencies of the other gases, given above, were determined using this section for Hg, and applying the gas-kinetic formula for the number of collisions at the pressure at which the resonance radiation is decreased to one-half its original value. In a continuation of the work of Stuart, Cario and Franck[4] observed that an increase of the temperature diminished apparently the quenching efficiency of N_2 so that at 750° forty mm of nitrogen would not affect the intensity of the resonance-radiation, while the same amount at room temperature would decrease it to one-third. To explan this curious behavior they applied a hypothesis of Joffé and Franck, according to which the life of the metastable 2^3P_0 atoms formed by collisions of the second kind of the resonance atoms with N_2 would end at higher temperatures mainly by collisions of the first kind with high-speed gas molecules, which would bring them back to the resonance level; the quenching due to collisions of the second kind bringing atoms down to the metastable level would be neutralized by collisions of the first kind which restore the atoms to the original excited level. Foote[5] applied the same consideration to the case of room temperature: If the non-quenching of N_2 at high temperatures (quenching efficiency $=0$) can be explained by collisions of the first kind of the metastable atoms, perhaps the small efficiencies observed by Stuart for rare gases can be explained in the same way. In fact, Foote calculated that at room temperature about 1/6000 of the molecules have a kinetic energy sufficient to perform a collision of the first kind with a metastable atom bringing it to the resonance level and since the life of the metastable atom is known to be about or larger than 6000 times the life of the resonance atom, collisions of the first kind may account completely for the apparent low efficiencies of Stuart. Foote assumed then, that every collision of a resonance atom with any foreign gas molecule is effective and is a collision of the second kind, which brings the atom either to the normal level (case of H_2) or to the metastable level 2^3P_0 (case of N_2, A, He, etc.). At the metastable level the atoms accumulate, because of their long life, until they are brought up again to the resonance level by a collision of the first kind; some of the metastable atoms will die before that happens, owing to collisions of the second kind with impurities and to formation of Hg_2 molecules. The quenching observed by Stuart with rare gases is then according to Foote only due to the presence of impurities (H_2 or O_2) and to the formation of molecules. If we increase the temperature of the foreign gas, that is the number of high-speed molecules, the probability for a metastable Hg atom to suffer a collision of the first kind will increase exponentially while the probabilities of meeting an impurity or of forming a Hg_2 molecule will increase only with the square root of the temperature, so that above a certain temperature the two last processes will be negligible in comparison with the first and no quenching of the resonance radiation will

[4] G. Cario u. J. Franck, Zeits. f. Physik **37**, 619 (1926).
[5] P. D. Foote, Phys. Rev. **30**, 288 (1927).

take place; the excited atoms will simply play between the resonance and the metastable levels but when they go down to the normal level they will emit the resonance line. This is what Cario and Franck observed.[6] From the hypothesis outlined above Foote developed a theory which was capable of reproducing the curves of Stuart by assuming the necessary amount of impurities and the necessary rate of formation of Hg_2 molecules for each case.

The Ratio f in Foote's Theory and the Diameter of the Excited Atom

Stuart obtained his value 3.4 for the ratio of the radius of the excited to the normal atom by assuming 100 percent quenching efficiency for the case of oxygen; Foote calculated this same ratio to be 1.15 assuming 100 percent efficiency for hydrogen, ignoring the apparently higher efficiency of oxygen, and introducing a factor f in his formula, which takes care of the re-absorption of part of the resonance radiation in the same resonating Hg-vapor. Foote's calculation for the case of H_2 is illustrated by the diagram reproduced here (Fig. 1).

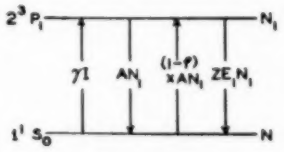

Fig. 1. Diagram illustrating Foote's calculation for H_2.

From the γI quanta of primary light absorbed, AN_1 are emitted as resonance radiation and $Z E_1N_1$ are used for collisions of the second kind if Z is the number of collisions and E_1 the efficiency of them; from the AN_1 quanta radiated fAN_1 escape the vessel and $(1-f)AN_1$ are re-absorbed in it.

In the stationary case therefore

$$AN_1+ZE_1N_1=\gamma I+(1-f)AN_1 \quad \text{and} \quad N_1=\gamma I/(fA+ZE_1) \tag{1}$$

Now, fAN_1 is the observed resonance radiation and if we call J the ratio of it to the absorbed radiation γI, we have

$$J=fAN_1/\gamma I=1/(1+ZE_1/fA) \tag{2}$$

Assuming with Foote that every collision with hydrogen is effective ($E_1=1$) we have

$$J=1/(1+Z/fA). \tag{3}$$

Now to apply this formula to Stuart's results it is necessary to make an estimation of the factor f. Foote estimates that from the resonance radiation one-half is re-absorbed in the vessel in the case of Stuart and puts $f=1/2$ in

[6] O. Oldenberg, Zeitz. f. Physik **49**, 609 (1928) has found recently that the quenching due to argon *increases* about five times if we raise the temperature to 750°, while with nitrogen, as found by Cairo and Franck it decreases to zero. This behavior of argon is difficult to understand and seems to be in contradiction with other evidence. It is possible that it may be due simply to some impurity which develops in the tube when heated. Oldenberg found namely (see footnote, p. 611, l.c.) that in some cases even N_2 showed a higher quenching power at 750°, but he disregarded this result because it contradicted the previous result of Cario and Franck.

his following calculations. But he does not consider what occurs with the re-absorbed radiation. This is what we shall do. Let us consider the resonance vessel R (Fig. 2) illuminated with parallel or slightly convergent light I and observed in the direction J from a certain distance, large as regards the diameter of R. Let us suppose first that the foreign gas pressure is zero, that is, that there are practically no quenching collisions. Then the whole absorbed and re-absorbed intensity will be radiated sooner or later as spherical waves with centers inside R and the factor f will be equal to 1. Let us suppose, second, that we have several mm of hydrogen in R, that is, that the resonance radiation is reduced to a small fraction by collisions of the second kind, then from the emitted resonance radiation one-half will be re-absorbed before leaving the vessel as calculated by Foote, and this half will be practically destroyed by collisions of the second kind, so that only the first half will be observed and f will be equal to *one-half*. The value of f depends then on the quenching coefficient J and lies between 1/2 and 1. The following series gives the value of f as a function of K where

Fig. 2.

$$K=1/(1+Z/A) \tag{4}$$

is the ratio of the excited atoms that emit resonance-radiation,

$$f=1/2+K/4+K^2/8+\cdots+K^n/2^{n+1}+\cdots. \tag{5}$$

We see that for $K=1,\ 1/2,\ 0$, $f=1,\ 2/3,\ 1/2$. Foote considered only the first term of the series. For the case of equal probability of emission and collision of the second kind ($K=1/2$), $f=2/3$, and for the case of reduction of the resonance radiation to 1/2, ($J=1/2$), $f=0.705$ and $K=0.585$, value calculated by successive approximations. The lower curve of Fig. 3 gives f as a function of K, calculated according to the series (5) and the upper curve represents f as a function of J, obtained by successive approximations using formula (3) and (4) and the previous curve.

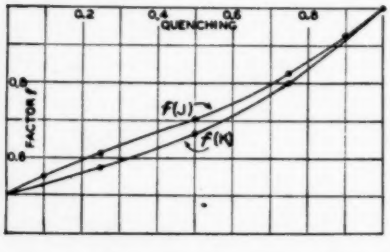

Fig. 3. Values of f as function of quenching coefficient J and of K.

If we calculate now the collision radius of the excited Hg atom using $f=0.705$ in formula (3) given above, the known gas kinetic formula for the number Z of collisions (formula 7) and the half pressure 0.217 mm found by Stuart for H_2, we obtain $r'_{Hg}=2.91\times10^{-8}$ cm, and since the radius of the normal atom is $r_{Hg}=1.80\times10^{-8}$ it is $r'=1.62\times r$. The radius 2.91×10^{-8} cm for the excited Hg atom is larger than the one calculated by Foote (2.03×10^{-8}) but two times smaller than the value 5.95×10^{-8} of Stuart. We shall use this newly calculated radius in the following considerations.

The Case of Oxygen

One objection made against Foote's theory[7] is that he ignores the fact that oxygen seems to have a greater quenching efficiency than hydrogen. Cario in 1922, who first calculated the radius of the excited Hg atom, already suspected that the quenching efficiency of air in Wood's original experiments in 1912 may have been due in part to a partial oxidation of the mercury vapor, and for this reason he went over to the use of rare gases in quenching experiments. This suspicion has been plainly proved in the work of Wood and Gaviola[8] from the conditions for the appearance of the forbidden line 2656 of Hg. There they found that if the illumination of the resonance tube is sufficiently strong, the admission of a few thousandths mm of oxygen is sufficient to destroy completely all fluorescence, including the resonance radiation of 2537. The same amount of hydrogen did not produce any noticeable effect upon the resonance-radiation. Oxygen would appear to have in this case an efficiency many hundred times higher than that of hydrogen. But Gaviola and Wood found also that the absorption of the primary light disappears at the same time, showing that no atomic mercury vapor is present in the tube. The explanation of this curious phenomenon is that mercury-oxide is formed as a result of the excitation of the mercury atoms, and the velocity of this oxidation is proportional to the intensity of the illumination. If the illumination is weak as in the case of Stuart, the oxidation will be slow and the mercury vapor will be partly replaced by the evaporation of the mercury drop contained at the bottom of the tube; if the illumination is strong as in the case of Wood and Gaviola the whole Hg vapor is oxidized in a fraction of a second and the new evaporating vapor is immediately destroyed as soon as it enters the illuminated zone. The apparent quenching efficiency of oxygen depends then on the intensity of the illumination. The reaction involved is probably[9]

$$Hg'+O_2\rightarrow Hg+O_2' \; ; \; O_2'+O_2\rightarrow O_3+O \; ; \; O_3+Hg\rightarrow O_2+HgO \; ; \; O+Hg\rightarrow HgO$$

Every excited Hg atom is thus capable, under favorable conditions, of producing two mercury-oxide molecules. This accounts satisfactorily for the anomalous behavior of oxygen.

The Efficiency of Quenching Collisions

The assumption made by Foote is that collisions of atoms in the resonance-level with gases are always effective and that collisions of metastable atoms are either completely inefficient in the case of rare gases and N_2, or completely effective in the case of H_2 and O_2, that is, if we call E the efficiency, that E can either be 1 or 0 but can not assume an intermediate value. This assumption appears too simple to be true. In fact, CO, for instance, has clearly some efficiency in destroying metastable atoms, but this efficiency is

[7] See for instance, M. W. Zemansky, Phys. Rev. **31**, 812 (1928).
[8] R. W. Wood and E. Gaviola, Phil. Mag. **6**, 271 (1928).
[9] E. Gaviola and R. W. Wood, Phil. Mag. **6**, 1191 (1928).

by no means as large as the efficiency of H_2 or O_2[10], which means that E in this case has a value actually between 0 and 1. Foote himself found that for the formation of Hg_2 molecules by collisions of metastable atoms with normal ones he had to admit an efficiency of about 0.07 in contradiction with his general assumption of "100 percent efficiency in all processes." Furthermore in a recent paper by Gaviola and Wood,[9] we have seen that collisions of resonance atoms with water molecules lead in most of the cases to formation of metastable atoms but in some of them to dissociation of the H_2O molecule into H and OH and still in some other cases to formation of a ($Hg-H_2O$) complex molecule, which shows that neither of these processes can have 100 percent efficiency. Another hint making probable that the efficiency of argon is neither 0.002 as calculated by Stuart nor 1 as assumed by Foote, is given by the results of Donat;[11] he illuminated a mixture of Hg and Tl vapor with 2537 and measured the increase of the intensity of the Tl lines when argon was admitted to the tube. Donat found that all lines reach a maximum at an argon pressure of 40 mm. Orthmann and Pringsheim[12] pointed out that since the pressure at which 2537 is reduced to 1/2 by argon is 240 mm according to Stuart, it was difficult to understand why a maximum is reached so far below the half-pressure. They tried to explain it by assuming that the excited Tl atoms were strongly quenched by the admitted argon.

On the other hand, if we assume with Foote an efficiency 1 for argon collisions, we ought to expect the maximum in the intensity of Tl lines at pressures of a few millimeters, which does not take place according to Donat's results. That the efficiency of A collisions is smaller than the efficiency of N_2 ones is shown by the investigation of Loria[13] on the photosensitized fluorescence of thallium vapor. Loria compares the increase of the thallium lines due to the admission of argon and of nitrogen and he finds that "at very low pressures · · ·the effect of N_2 may be even much stronger than that of A. It is enough to introduce into the tube a small fraction of a millimeter of carefully purified N_2 (about 2×10^{-3} mm) to make the whole window shine with vivid, very bright soft green light" (p. 579, l.c.). Now, at very low pressures (less than 1 mm) collisions of the first kind can be neglected, as we shall see presently, and therefore the amount of metastable atoms of which the intensity of the green thallium light is an indicator (metastable atoms produced by collisions of the second kind with the foreign gas) is simply proportional to the efficiency of the last collisions. The observation of Loria shows then that the efficiency of nitrogen collisions with resonance atoms is "much stronger" than that of argon collisions. But we can calculate the efficiency of quenching collisions for each foreign gas simply from the curves of Stuart.[3] The reason Stuart found too small efficiencies for the rare gases is that he used only the pressure at which $J=1/2$ for calculating them. At

[10] E. Gaviola, Theory II, Phil. Mag. **6**, 1167 (1928).
[11] K. Donat, Zeits. f. Physik **29**, 345 (1924).
[12] W. Orthmann and P. Pringsheim, Zeits. f. Physik **35**, 626 (1926).
[13] S. Loria, Phys. Rev **26**, 573 (1925).

such pressure collisions of the first kind with high-speed molecules bring metastable atoms back to the resonance level and compensate in part or in full the quenching action of the foreign gas. Since at room temperature 1 in 6000 molecules has a speed sufficient to bring a metastable atom up to the resonance level the necessary condition for the occurrence of the process to an appreciable extent is that the metastable atoms live at least 6000 times longer than the resonance ones, that is about 10^{-3} sec. (as pointed out by Foote). Now at pressures below a few millimeters the life of the metastable atoms is shorter than this because of collisions of the second kind with the walls of the tube: for the diffusion rate towards the wall is proportional to the inverse pressure and at low pressures a large number of metastable atoms will collide with the walls before they live 10^{-3} sec. Their life at 10^{-3} mm pressure (saturated Hg vapor at room temperature) cannot be much longer

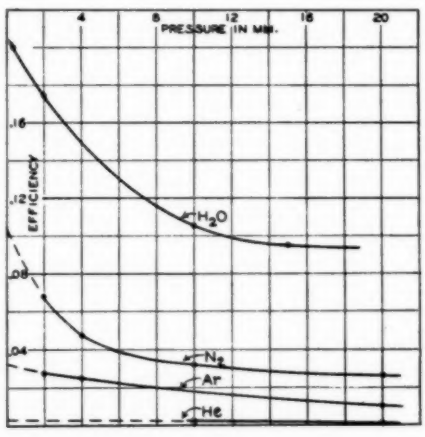

Fig. 4. Efficiency curves for H_2O, N_2, A and He.

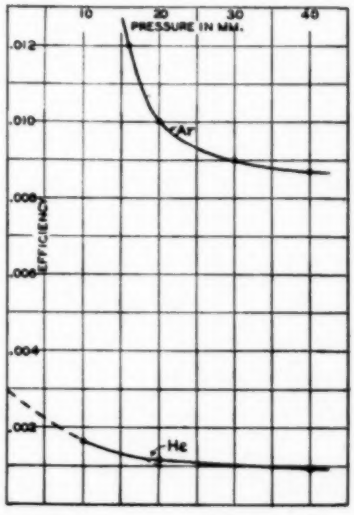

Fig. 5. Efficiency curves for A and He.

than 3×10^{-5} sec. (the mean distance from the wall is 0.5 cm and the mean velocity 1.7×10^{-4} cm/sec.). The influence of collisions of the first kind will then disappear as we lower the pressure. If we calculate then the efficiency as a function of the pressure from Stuart's measurements we should expect it to increase as the pressure diminishes and to approach a value for $p=0$ which is the real efficiency coefficient. From formula (2) we obtain for the efficiency

$$E_1=fA(1-J)/JZ \tag{6}$$

where J is the value measured by Stuart, f the corresponding re-absorption factor (Fig. 3), A the emission-probability of $2537=1/(1.1\times10^{-7})$, and Z the number of collisions per sec.

$$Z=2.608\times10^{-22}\times\sigma^2\times p\times((m+m_1)/m\times m_1)^{1/2} \tag{7}$$

if σ is the sum of the radii of the two colliding molecules and p the pressure in mm. The efficiency curves for H_2O, N_2, A and He are given in Figs. 4 and 5. We see that the efficiencies really increase as the pressure goes down which proves the assumption that the life of the metastable atom *decreases* at low pressures because of collisions with the walls of the vessel. It is very interesting that the life of metastable atoms can be lengthened by admitting a foreign gas. This effect has been expected by several investigators[14] but it is shown for the first time here, as a result of experiments, that it really exists.*

Extrapolating the curves to zero pressure we obtain the following efficiencies: 0.2 for H_2O, 0.1 for N_2, 0.03 for A, and 0.003 for He. This means that 1 out of 5 collisions with water vapor, 1 out of 10 with nitrogen, 1 out of 33 with argon, and 3 out of 1000 with helium, are quenching collisions. This explains why at low pressures nitrogen is better than argon in increasing the thallium fluorescence as found by Loria and why water vapor is better than nitrogen for developing the "forbidden" line 2656 as found by Wood and Gaviola.

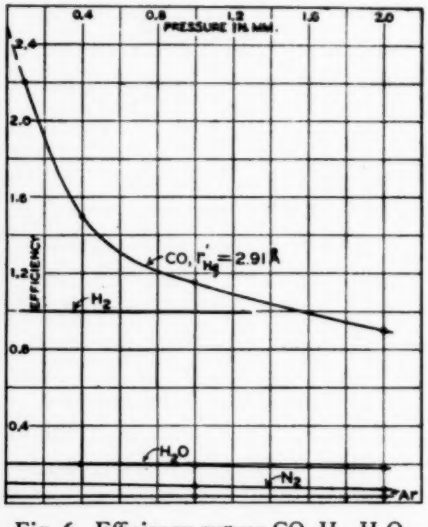

Fig. 6. Efficiency curves CO, H_2, H_2O, N_2, A.

The efficiency curve for H_2 ought to be a horizontal line since no collisions of the first kind can be expected in this case. Fig. 6 shows that this is actually the case.

If we plot now the efficiency curve for CO we obtain a surprising result (Fig. 6); CO has a higher quenching efficiency than hydrogen and the extrapolated value for zero pressure is 2.5.

Table I gives in the second column the radii used; in the third column, the number of collisions Z obtained by formula (7) assuming a radius $r = 2.91 \times 10^{-8}$ cm for the excited mercury atom, and in the fourth the efficiencies obtained from Figs. 4, 5, and 6, extrapolating to zero pressure. We shall refer presently to the two last columns.

The Case of CO

In the case of CO we find the surprising result that the efficiency of quenching collisions increases far beyond 1 as the pressure diminishes and it approaches a value 2.5 for $p = 0$. For the calculation of this curve we have used $r_{CO} = 1.6 \times 10^{-8}$ cm as radius of the CO molecule as given by Landolt-Börnstein and $r_{Hg'} = 2.91 \times 10^{-8}$ cm for the excited mercury atom as obtained

[14] See for example T. Asada, R. Ladenburg and W. Tietze, Phys. Zeits. **29**, 549 (1928).

* Note added in proof. In a recent paper by M. L. Pool (Phys. Rev. **33**, 22 (1929)) the existence of this effect has been shown in a more direct way.

in a former paragraph. Since an efficiency can not, by definition, be greater than 1 it is necessary to find an explanation for this result. Now the radius 1.62-fold normal attributed to the excited mercury atom was calculated under the assumption that the efficiency of *hydrogen* collisions was equal to 1. This assumption was arbitrary and it was made because hydrogen seemed so far to have the greatest quenching efficiency, which, as we see now, is not the case: actually CO has a greater quenching efficiency than H_2. If we define now the efficiency of CO collisions as unity we must assume

TABLE I. *The quenching efficiencies of various gases for the resonance radiation of Hg as calculated from two values of the radius of the excited Hg atom.*

Gas	Radius	$Z(r_{Hg'}=2.91A)$	Efficiency $p\to 0$	$Z(r_{Hg'}=5.5A)$	Efficiency
H_2	1.09×10^{-8} cm	$3.0\times10^{+7}\,p$	1.	$8.16\times10^{+7}\,p$	0.4
H_2O	$1.36\times$ " "	$1.17\times$ " "	0.2	$3.0\times$ " "	0.08
N_2	$1.58\times$ " "	$1.05\times$ " "	0.1	$2.6\times$ " "	0.04
A	$1.43\times$ " "	$0.85\times$ " "	0.03	$2.16\times$ " "	0.01
He	$1.00\times$ " "	$2.8\times$ " "	0.003	$7.7\times$ " "	0.001
CO	$1.6\times$ " "	$1.07\times$ " "	2.5	$2.64\times$ " "	1.

that the radius of the excited mercury-atom is larger than the one used before; a radius equal to 5.5×10^{-8} cm, which is about three times the radius of the normal atom gives us in fact an efficiency equal to 1 for CO. This radius is about twice as large as the one calculated in the case of H_2. If we assume that the radius 5.5×10^{-8} cm is the *real* radius of the excited mercury atom we must conclude that the efficiency of hydrogen collisions is less than one-half and accordingly diminish the efficiencies of the other gases. The two last columns of Table I are calculated under this assumption. But this conclusion is arbitrary: the collision section of the excited mercury atom may be different for each particular gas. The experiments give us only a value for the product E_1Z (See formula (2)) where Z is the number of collisions and E_1 the efficiency of them, and Z is proportional to σ^2 (formula 7) if σ is the sum of the radii of the two colliding molecules. We measure then the product $E_1\,\sigma^2$ and in order to calculate the radius sum σ we make an arbitrary assumption about E_1 for one particular gas and then apply this value σ to all the other gases and calculate their efficiencies. This was the course followed by Stuart and by the author in the former calculations. But we could also do the contrary: we could assume $E_1=1$ for all the gases and calculate a collision-section for each of them, but if we do so we obtain for gases like N_2, A, and He, collision sections many times smaller than the gas kinetic ones which is undesirable to assume. In these cases therefore we must assume $E_1<1$. But in the cases of H_2 and CO (and perhaps O_2) where assuming $E_1=1$ the collision section turns out to be greater than the gas kinetic one, there is no need and there is not purpose in postulating $E_1<1$. An efficiency smaller than one would simply mean a still larger collision section. We can in these cases assume a different radius of the excited atom for each particular gas.

It seems of course desirable to assume *one* radius for the excited atom as we have one for the normal atom and to express the different behavior of gases in terms of efficiency-coefficients, but we have seen the danger of such an assumption; we may always find a new type of collision in which the efficiency appears to be greater than 1, which would oblige us to increase the assumed radius and parallel with it to decrease all the efficiency coefficients for the other gases.

The simplest way seems then to maintain the gas kinetic radius of the normal also for the excited atom in all the cases in which doing so, the efficiencies turn out to be smaller than one, and when not, to assume a radius for the excited atom, larger than the gas kinetic one, for each particular case, so that the efficiencies in each case are unity. Table II is calculated this way. This assumption is of course also arbitrary.

TABLE II. *Quenching efficiencies of various gases for the resonance radiation of Hg.*

Gas	Radius	$r_{Hg'}$	Z	Efficiency
CO	1.6×10^{-8} cm	5.5×10^{-8} cm	$2.7 \times 10^{+7}\ p$	1.
H_2	$1.09 \times$ " "	$2.91 \times$ " "	$3.0 \times$ " "	1.
H_2O	$1.36 \times$ " "	$1.80 \times$ " "	$0.64 \times$ " "	0.4
N_2	$1.58 \times$ " "	$1.80 \times$ " "	$0.6 \times$ " "	0.2
A	$1.43 \times$ " "	$1.80 \times$ " "	$0.5 \times$ " "	0.05
He	$1.00 \times$ " "	$1.80 \times$ " "	$1.4 \times$ " "	0.006

The results of the present investigation make necessary a revision of Foote's theory and on the other hand allow us to predict the life and the number of metastable atoms as a function of the foreign gas pressure under different conditions, all of which will be dealt with in one or two subsequent papers, which will appear shortly.

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WASHINGTON, D. C.
November 5, 1928.

PERSISTENCE OF λ2537 IN MERCURY AT LOW PRESSURES

By Harold W. Webb and Helen A. Messenger

Abstract

The persistence of λ2537 excited by electron impact in mercury vapor was measured for vapor pressures corresponding to the temperature range 78° to −19°C, using the alternating potential method previously described by one of the authors. Between 78° and 17°C this persistence was found to vary inversely as the first power of the pressure, and not inversely as the square of the pressure as predicted by theories of the diffusion of radiation by repeated absorption and re-emission. A modified theory of diffusion of radiation seems necessary to explain the persistence which is much too small to be explained as depending upon the life of the metastable atoms. As the pressure is lowered the persistence approaches a limiting value of the order of 10^{-7} seconds.

The life of λ1849 was found to be less than 3×10^{-9} seconds. A radiation process probably associated with the 7.1 break in the critical potential curves was found to have a life of 1/470000 seconds. It is suggested that this is the life of an infra-red transition to the 6.7 volt level, followed by the radiation of 1849. Another process associated with an excitation potential lying between 5 and 6 volts had a life of about 1/120000 second.

IT HAS been shown by one of the authors[1] that with a modified Lenard tube having a nickel or aluminum photoelectric plate and a quartz filter separating the excitation and detecting systems, the critical potential curves of mercury are due to radiations of wave-lengths less than 2700 and greater than 1650A. The quartz filter eliminated the "photoelectric" effect of the metastable atoms which with the surfaces used was much greater than the true photoelectric effect due to radiation. The radiations detected were as follows: (a) 2537A, (b) 1849A, (c) radiation of wave-length between 2500 and 2200A, probably the molecular band 2338-2313A, and (d) radiation of wave-length between 2200 and 1650A, probably the molecular band 2140A. The other radiations excited below the ionization potential do not directly affect the plate photoelectrically as they lie well above its photoelectric long wave-length limit.

In the present experiments the radiations associated with the critical potential curves were studied further as regards their persistence after excitation. In particular the persistence of 2537 was measured for vapor pressures corresponding to the temperature range 78° to −19°C. The presistence of this line for pressures corresponding to the temperature range 130° to 60°C had already been carefully studied by Zemansky.[2] By means of a rotating sectored disk he intermittently illuminated with 2537 the

[1] Helen A. Messenger, Phys. Rev. **28**, 962 (1926).

[2] M. W. Zemansky, Phys. Rev. **29**, 513 (1927).

front face of a quartz cell containing mercury vapor and by a second synchronous disk measured the emission of this line from the rear face as a function of the time after the illumination was cut off. His results did not agree with the simple theory of diffusion of radiation by repeated absorption and re-emission, which has been developed in detail by Milne,[3] and he attempted to account for this by dissipative impacts. In particular the diffusion theory predicts a law of decay of the persistent radiation transmitted by the cell which is roughly exponential, with a constant inversely proportional to the square of the vapor pressure, while Zemansky found that, even at the lowest temperature at which he could make measurements (60°C), this constant varied very much less rapidly.

The method here employed for the measurement of the persistence of radiation is described at length in previous papers.[4] Briefly, this consists

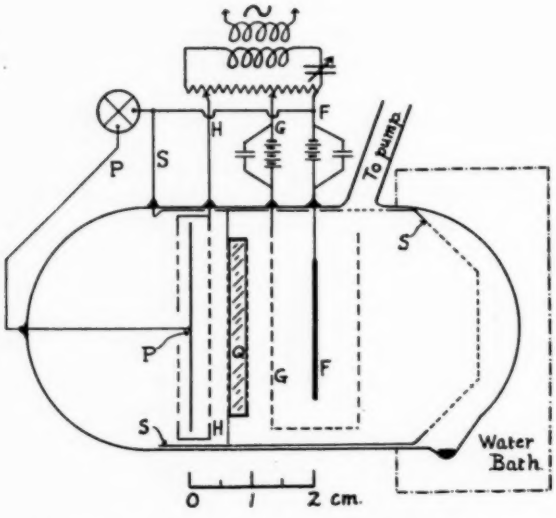

Fig. 1. Experimental tube and electrical circuits.

in exciting the radiation intermittently by applying an alternating potential between the hot cathode F (See Fig. 1.) and the excitation grid G the voltages being so arranged that excitation occurs only in the positive half-cycles. In phase with this is a second alternating potential applied between the detecting photoelectric plate P and the photoelectric grid H which permits photo-electrons to leave P only during the positive half-cycles and causes photo-electrons from H to go to P during the negative half-cycles. As the frequency of the alternating voltages is increased, since the radiation persists after its excitation, it holds over to some extent into the negative half-cycle and the electrometer current from P is reduced. From the variation of this current with the frequency, the persistence may be calculated.

[3] E. A. Milne, Journ. Lon. Math. Soc., No. **1**, (1926).
[4] H. W. Webb, Phys. Rev. **24**, 113, (1924); F. G. Slack, Phys. Rev. **28**, 1 (1926).

Apparatus

The tube used, which was similar to that described by Messenger as Tube I, (Reference 1, p. 964) is shown by diagram in Fig. 1. The oxide-coated hot cathode F was equipotential. The grids G and H were of nickel gauze, as was also the shielding electrode S. The plate was of nickel, polished but not degassed. The quartz window Q separated the excitation and detecting systems, permitting only radiation to pass, and blocking the metastable mercury atoms.

The vapor pressure was controlled by a water bath enclosing one end of the tube, where all the liquid mercury collected. The rest of the tube, including 30 cm of the pumping tube was superheated. To insure having the vapor pressure in the tube that corresponding to the temperature of the bath the pumping tube could be closed by a steel ball seated in a constriction. The bath could be held constant within one degree at temperatures ranging from 80° to −20°C, the low temperatures being obtained by salt and ice mixtures.

During observations a diffusion pump was operated continuously to prevent accumulation of traces of gas, which never exceeded a pressure of 0.0001 mm.

The electrical circuits were similar to those described by Webb.[4] They are shown schematically in Fig. 1. Special care was taken in the design of the oscillators and coupled circuits to insure approximately a sine wave-form for the impressed alternating potentials, as this is essential to the method.

Procedure

The cathode F was held constant at +4.5 volts and the shield S and the plate P were at ground potential. The voltage on G measured with respect to F will be described as follows; $G\text{-}F=a\pm b$, a being the fixed potential difference and b the peak value of the superposed alternating potential. The alternating potential used on H was from 3 to 4.5 volts in peak value.

The two tests for proper functioning of the tube and for wave-form described by Webb[4] (Reference 4, pp. 119-120) were used throughout.

With alternating potentials on both systems the ratio of the electrometer currents for high frequency C and for 60 cycles C_0 was determined as a function of the frequency (See Fig. 3.). This ratio R is used instead of the actual current to eliminate variations in emission and plate sensitivity. For all of the times of persistence met with in this work 60 cycles was equivalent to zero frequency, since no appreciable hold-over occurred at this frequency.

If we assume that radiation excited at time $t=0$ falls off according to the law $e^{-t/T}$; if, as was usually the case, the excitation of the radiation varies according to a sine law during the positive half-cycle of the alternating potential on $G\text{-}F$ and is zero in the negative half-cycle; and if the photoelectric current saturates very soon after reversal of the alternating potential $H\text{-}P$,

as was also the case, the current ratio, R, as a function of the frequency f is $R=C/C_0=[(1/T^2)+2\pi^2f^2(1\text{-}S)]\div[(1/T^2)+4\pi^2f^2]$, where S is the ratio of the positive and negative saturation currents of the H-P system for steady radiation. For $f=0$, (60 cycles), $R=R_0=1$. For $f=\infty$, $R=R_\infty=\frac{1}{2}(1\text{-}S)$. Let $R_{1/2}=\frac{1}{2}(R_0\text{-}R_\infty)$ and let $f_{1/2}$ be the corresponding frequency. We have $R_{1/2}=\frac{1}{2}[1+\frac{1}{2}(1\text{-}S)]=[(1/T^2)+2\pi^2f_{1/2}^2\ (1\text{-}S)]\div[(1/T^2)+4\pi^2f_{1/2}{}^2]$ which gives $1/T=2\pi f_{1/2}$. This gives a simple means of calculating the value of $1/T$ from the "R-frequency" curve. If two radiations with different decay rates are present this relation may be separately applied to the part of the current due to each.

With this method of measuring times of persistence it is difficult to obtain precision unless only a single radiation is effective at one time. It was there-

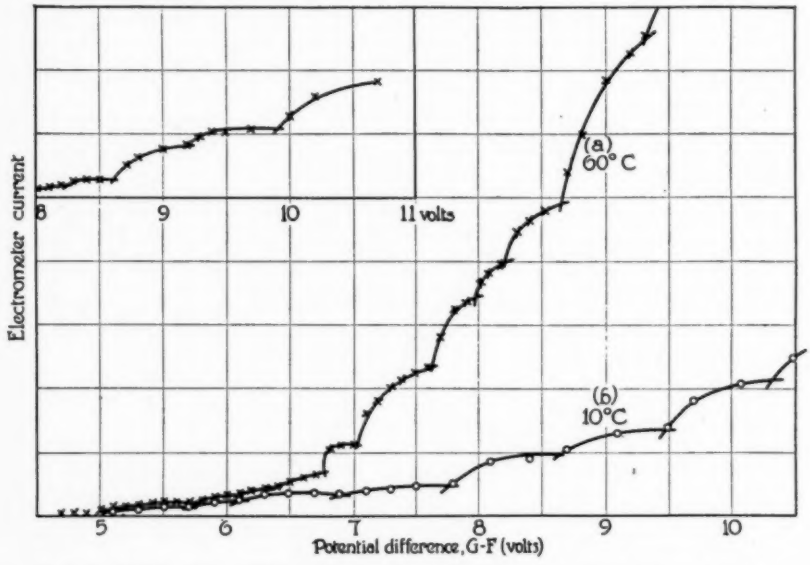

Fig. 2. Critical potential curves with experimental tube at 60° and 10°C. Corrected voltages are given.

fore important to vary the conditions until the radiation to be studied was predominant. This was accomplished in several ways; chiefly, by the variation of the G-F voltages, both fixed and alternating, and by changes in vapor pressure, which in particular had a marked effect on the strength of 2537 relative to that of the other radiations. Again, accidental variations of the plate sensitivity were sometimes a help in separating the radiations. The plate became at times quite insensitive to 2537 and radiations were then measurable which were masked when the plate returned to normal sensitivity.

Results

Fig. 2. shows two ordinary critical potential curves, taken with the tube at 10° and 60°C, respectively. As the quartz window eliminated the metastable atoms, these curves show how the total radiation affecting the plate

varied with the voltage on G. Fig. 3 shows three typical "R-frequency" curves taken with alternating potential on both G and H.

The measurements indicated that there were present in measurable amount four types of radiation. The outstanding one was the line 2537. This radiation is peculiar in that its persistence varies widely with the vapor pressure so that it was easily identified. A second group of radiations of which 1849 probably formed the most important part had a persistence too short to be measured with the apparatus which could not be used with frequencies greater than 3×10^6 cycles. There were found further two other types of radiations having life-times 1/470000 sec. and 1/120000 sec., respectively. Radiations such as 4047, 4358, etc., which are also excited below the ionization potential were not directly effective since the nickel was quite insensitive to wave-lengths greater than 3000A.

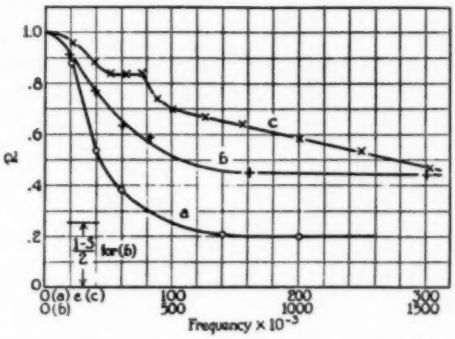

Fig. 3. R-frequency curves. *a*. 40°C, G—$F=5.4\pm1.3$; *b*. 22°C, G—$F=6.7\pm3.3$; *c*. 29°C, G—$F=8.1\pm2.0$.

Wave-length 2537. By trial it was found that the 2537 radiation could be best isolated from the other radiations by using exciting voltages below 6.7 volts. Consequently when possible the curves taken in studying it were with G-$F=5.4\pm1.3$ volts. Measurements of its persistence were made at temperatures covering the range 78° to −19°C. Fig. 3, Curve *a* shows the curve taken at 40°C, illustrating the type of curve obtained.

The assumption made above that the radiation reaching P decays according to the simple exponential expression $e^{-t/T}$ is incorrect if the radiation comes out by any kind of diffusion process. Such a process would be described by an equation the solution of which would contain an infinite series of terms of the exponential form with rapidly increasing negative exponents. The form of the exponents and of the coefficients of the terms would depend upon the geometry of the space in which the diffusion takes place. A solution of the ordinary type of diffusion equation for conditions approximating those in the experimental tube was made and it was found that the corresponding R-frequency curve calculated did not differ greatly from the curve for a simple exponential decay of the radiation. It does not decrease so rapidly at first but the rest of the curve is somewhat steeper than the simpler curve. The difference between the two types of curve is not sufficient, however, to differentiate between them with the present experimental curves. The precision of these is such that an equally good fit can be obtained with either type. Consequently the results of the present measurements are given in terms of $1/T$, the constant in the simple exponential expression computed as described above from $f_{1/2}$. It may be noted, however, that this value is practically equal to the exponential constant in the first term of the series obtained by the solution of the diffusion equation, in the case worked out being too small by about 10 percent.

In Table I, column 3, the values of $1/T$ so obtained from nine curves are summarized. Column 1 gives the corresponding temperatures of the liquid mercury in the tube, while column 2 gives the corresponding number of atoms per cc. Column 4 shows the exciting voltage *G-F*. In the last column appear estimates of precision and other comments.

TABLE I. *Persistence of λ2537.*

Temperature	Number of atoms per cc $\times 10^{-11}$	$1/T$	*G–F* volts	Remarks
−19°C	8.6	(10^7)	6.9 ± 4.6	$6\times10^6 < 1/T < 1.3\times10^7$
−10	26	6.3×10^6	6.7 ± 3.3	Precision 20%
0	77	5.0×10^6	6.7 ± 3.3	" 15%
7	160	2.3×10^6	5.4 ± 1.4	" 15%
17	410	1.3×10^6	5.4 ± 1.3	" 10%; complex curve
22	630	7.5×10^5	6.7 ± 3.3	" 15%; complex curve
40	2000	2.6×10^5	5.4 ± 1.3	" 10%
60	7700	7.9×10^4	5.4 ± 1.3	" 10%
78	22000	2.4×10^4	5.4 ± 1.3	" 15%

It will be noted that at the lower pressures, below 7°C, a higher *G-F* voltage than 5.4 ± 1.4 was used. This was necessary because the low vapor pressure resulted in small excitation. At these pressures the radiations other than 2537 were practically negligible in amount. At −19°C the energy excited was too small for precise measurement. The measurements obtained sufficed, however, to give an estimate of the value of $1/T$ for this pressure of about 10^7 sec^{-1}. At 17° and 22° the curves were each the result of mixed radiation. At 17°, 2537 was mixed with the radiation having the life time 1/120000 sec; at 22° it was mixed with about 25 percent of 1849. (See Fig. 3, curve *b*). The value of $1/T$ for the part due to 2537 was in each case obtained by a graphical analysis of the curve.

These results are plotted in Fig. 4, with $\log_{10}$ concentration as abscissas and $\log_{10}$ $1/T$ as ordinates. The 1000-fold variation in the values of $1/T$ and the 6000-fold variation in concentration make it inconvenient to plot them directly. Opposite each point on the curve is given the corresponding value of the temperature. The dotted portion at the lower right hand part of the figure was obtained by extrapolation from the results of Zemansky.[2] It was assumed that the present apparatus is roughly equivalent to the smaller of his cells which was 1.3 cm thick. This is of the right order of magnitude, as will be seen from Fig. 1. The geometry of the tube is too complex for a more precise computation.

The life of the excited 2^3P_1 state in the mercury atom has been measured by a variety of methods and the value 10^{-7} sec. is the best average of the values found. (Cf Zemansky,[2] p. 519). This life must be the limiting value of the persistence of 2537 as the pressure diminishes and consequently the curve has been drawn asymptotic to this ordinate. The curve indicates that for 10^{11} atoms per cc the time of persistence is practically the life of the excited state and that at this pressure no persistence due to absorption and re-emis-

sion or any similar process delays the radiation in passing to the detecting photoelectric surface.

The curve shows that for no pressure does $1/T$ vary inversely as the square of the concentration of atoms. This would be indicated by a slope parallel to the line *CD*. The results therefore do not agree with Milne's theory of diffusion of radiation by the process of repeated absorption and re-emission, at least in its simplest form, since this requires $1/T$ inversely proportional to the concentration squared. For the region of concentration corresponding to the temperature range 78° to 17°C, $1/T$ varies very nearly inversely as the first power of the concentration, as indicated by the coincidence of the curve with the 45° line *AB*.

In spite of the failure of the simple form of the theory of diffusion of radiation to explain the variation of the persistence with concentration, it still seems most probable that for pressures corresponding to temperatures

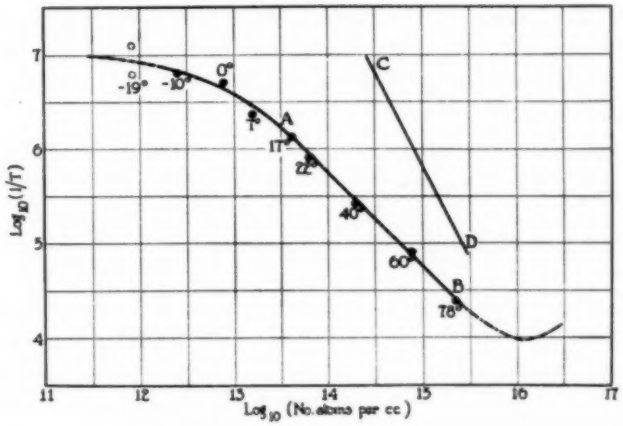

Fig. 4. Persistence of λ2537 vs. concentration.

between 78° and 17°C, we have to deal with a diffusion process consisting of absorption and re-emission. It does not seem possible to explain the persistence in this region as due to the formation of metastable atoms, which carry the excitation energy until as the result of impact they are brought back to the 2^3P_1 state from which they radiate 2537. At 40°, for example, Coulliette[5] has shown that the average life of the metastable atom in the present tube should be of the order of 1/10000 sec., while the average persistence of 2537 actually observed was 1/260000 sec. It may be noted further that at this temperature the interval between impacts is nearly ten times as great as this average persistence of 2537. We can not therefore connect the radiation persistence with the longer lived metastable atoms. Some modified form of the theory of diffusion of radiation by repeated absorption and re-emission seems necessary to explain the present results. It is probable that the present theory fails to describe the facts because it does not take

[5] J. H. Coulliette, Phys. Rev. **32**, 636 (1928).

into account the effect of the breadth of the absorbed line, and of possible processes which may result in the gradual change in the width of the line as the quantum passes from atom to atom. New experiments are in progress to test this directly.

For concentrations corresponding to temperatures below 17°C, the curve deviates from the straight line, as is to be expected since $1/T$ can never exceed the life time of a single excitation which is about 10^{-7} sec. If we regard the persistence as some kind of diffusion process this region corresponds to the condition in which the "mean free path" is nearly equal to or less than the dimensions of the space in which the process is taking place. Under such conditions the diffusion is always slower than is indicated by the diffusion equation as derived for small free paths. For example, at zero degrees we would have on the average only two emission processes and only one absorption of a quantum on its way to P, and we should not expect the ordinary equations of diffusion to apply. For concentrations corresponding to temperatures greater than 78°C the process of persistence is obviously more complex. Zemansky has already discussed the possible causes of this.

From the measurements at 0° and 7° the atomic absorption coefficient was estimated to be of the order of 10^{13}.

Other excitations. When *G-F* voltages with peak values well in excess of 8.3 volts were used the frequency-current curves failed in many cases to drop to the theoretical lower limit $R_\infty = \frac{1}{2}(1\text{-}S)$, even with the highest frequencies available. This was due to the presence of radiation having a life too short to be affected by the frequencies used, estimated as less than 3×10^{-9} sec. From the voltages at which this radiation became prominent it was concluded that it was the line 1849. Eldridge[6] and Messenger (Reference 1, p. 594) both found a rapid increase in the rate of excitation of this line as the exciting voltage increased beyond 8.3 volts. Fig. 3, Curve *b* shows one case in which 1849 is one-fourth as intense as 2537, as measured by the photoelectric current due to each. This curve should eventually fall to $R_\infty = 0.25$, but at $f = 1.5\times10^6$ the part due to 1849 has shown no tendency to decrease.

For *G-F* peak voltages above 7 volts, another type of excitation was found for which $1/T = 470000$ sec.$^{-1}$. The curves showing this were best developed for $G\text{-}F = 5.4 \pm 3.8$ volts. (When the peak voltage considerably exceeded 9.2 volts, 2537 again became very prominent.) The new type of radiation was measured at 60°, 55° and 40°C with practically the same result, so that its life does not depend on the vapor pressure. To determine the minimum voltage at which this radiation is excited the following test was made. With the tube at 60°, and $G\text{-}F = 5.4$ plus a variable alternating voltage of 80000 cycles, and alternating voltage on *H-P*, Curve *a* of Fig. 5 was obtained for the values of R, plotted against peak value of *G-F*. The frequency 80000 was selected since at 60°C the 2537 radiation gives practically $R_\infty = 0.25$, while this 470000 radiation gives the value $R = 0.62$. The

[6] J. A. Eldridge, Phys. Rev. **23**, 685 (1924).

curve, starting at $R=0.27$, increases slowly to 7 volts and then rises rapidly, finally reaching the value 0.62 at 8.3 volts. This is interpreted as follows: 2537 is predominant below 7 volts; at 7 volts the 470000 radiation begins to increase and at 8.3 volts is itself predominant. (The 60° curve for $G\text{-}F=5.4\pm3.8$ shows practically only this radiation.) The slight upward slope of the curve below 7 volts may be accounted for by 1849 which is excited above 6.7 volts. This is confirmed by measurements recorded as the dotted part of the curve which was taken at 500000 cycles for which frequency both 2537 and the 470000 radiation give theoretically $R=0.26$. The difference between this and the observed value is presumably due to 1849.

The point of appearance of the 470000 radiation corresponds closely with the 7.1 break in the critical potential curve. Messenger found that this break was practically absent when these curves were taken through a calcite filter, indicating that part of the radiation associated with this break which is capable of affecting the nickel photoelectric plate lies between 2200 and 1650 and is probably 1849. We conclude therefore that the life time 1/470000 sec. is that of the transition from the 7.1 level to the 6.7 level. The radiation, if any, accompanying such a transition would be in the infra-red and would not affect the plate. The 1849 radiation resulting from the transition down from the 6.7 level accounts for the photoelectric current, but as the life of 1849 radiation is very short the life of the first transition is the one measured. The fact that this life time is independent of pressure makes it improbable that metastable atoms or radiation diffusion play any part in this persistence.

That this radiation is associated with the 7.1 break is in accord with the fact that it was most prominent for pressures corresponding to temperatures greater than 30°C. The critical potential curves show that the radiation associated with the 7.1 break is a much greater fraction of the total radiation at high temperatures than at low. (Cf Fig. 2, Curve *a* at 60 and Curve *b* at 10°C.)

Another radiation was observed having a value of $1/T$ roughly equal to 120000 (between 100000 and 200000). It was never isolated sufficiently for precise measurement, but usually was masked by 2537 and manifested itself only as an irregularity in the curve. (See Fig. 3, Curve *c*.) In several cases it stood out rather prominently owing to some condition which temporarily rendered the photoelectric surface quite insensitive to 2537. This condition was however transitory and no satisfactory curve for this radiation was obtained. To determine the break in the critical potential curve with which this radiation is associated, Curve *b* Fig. 5, similar to Curve *a*, was taken at 0°C with $G\text{-}F=5.4$ plus a variable alternating potential of 37500 cycles. At this temperature and for this frequency 2537 gives $R=100$ and the 120000 radiation gives $R=0.35$ (approximately). While the value of R for 6 volts peak

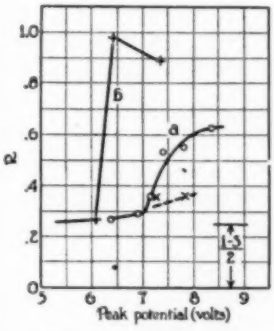

Fig. 5. *a*. Peak value of $G-F$ vs. R. Solid line, frequency 80,000; dotted line, frequency 500,000. *b*. Peak value of $G-F$ vs. R. Frequency 37,500.

value of G-F is lower than calculated, the error being probably due to the very small radiation at this voltage, the curve rises sharply to a value of nearly unity at 6.4 volts indicating that below 6 volts the 120000 radiation is a large part of the total but that above 6 volts 2537 becomes predominant. The curve drops to 0.95 at 7.4 volts due probably to the increase in the 470000 radiation.

These results indicate only that this 120000 radiation is excited below 6 volts. It seems probable that it is either one of the molecular bands excited between 5 and 6 volts or that what was measured was the life of a transition to the 4.86 volt level giving itself no radiation capable of affecting the nickel plate but followed by 2537.

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THE EXCITATION OF SODIUM BY IONIZED MERCURY VAPOR

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Abstract

Excitation of sodium by excited and by ionized mercury vapor.—The excitation of the sodium spectrum by ionized mercury distilling from an arc was studied in a tube in which conditions were under control. An auxiliary electrode in the stream of mercury vapor was used to increase the number of excited atoms at the point of observation until the excitation due to them predominated over that due to the ions. The spectrum produced by excited mercury atoms was thus compared with that due to mercury ions. The spectrum due to the excited atoms showed the marked "resonance" effect shown earlier by Beutler and Josephy. The spectrum due to mercury ions also showed excitation corresponding to the excitation energy of the metastable mercury atom. This may be accounted for as due to metastable atoms formed as the result of recombination of mercury ions. An alternative explanation is that the excitation of a sodium atom by a mercury ion is by a three body impact involving a mercury ion, a sodium atom and an electron. This was suggested by the fact that when sodium is introduced into the ionized mercury there is a strong enhancement of the mercury lines originating at the two 3*S* levels, which seems to be best explained as due to three body impacts. It seems probable that both this and the above process are of the same nature. It was noted further that the spectrum excited by ionized mercury resembles the chemiluminescence spectrum resulting from mixing sodium and mercuric chloride vapors. The spark line of mercury 3984, not previously found in the luminous mercury stream, was found when sodium was present.

RAYLEIGH[1] has shown that the ionized luminous vapor distilled from a metallic arc will on mixing with a second metallic vapor optically excite it. In his experiments the arc was formed in a cylindrical vessel one base of which was the anode. The luminous vapor passed through a hole in this anode and met a similar jet from an opening in the side of a nearby furnace in which the second vapor was heated. In addition to the well-known afterglow spectrum of the first metal, arc lines and in several cases spark lines of the second vapor were observed due to the action of the luminous vapor on the unexcited vapor. Rayleigh observed that except in a few cases the values of the energy of excitation of the lines excited in the second vapor were less than the ionization energy of the first vapor.

Since in Rayleigh's apparatus the anode of the arc was about one centimeter from the region of excitation it is probable that there were other sources of excitation besides the ions. In the case of luminous mercury vapor we would expect excitation by excited atoms in the $2^3P_{0,1}$ states. Such excitation has been shown by Beutler and Josephy,[2] who excited the mercury

* The appointment of the senior author as Ernest Kempton Adams Fellow enabled him to secure the collaboration of Dr. Wang.

[1] Rayleigh, Proc. Roy. Soc. **A112,** 14 (1926).

[2] Beutler and Josephy, Naturwiss. **15,** 540 (1927).

line λ2537 by radiation in a mixture of mercury and sodium vapors and found a maximum of excitation for the sodium lines whose excitation energies agreed most nearly with that of 2537. They found further that, when metastable atoms (2^3P_0) were present in large numbers, there was a second maximum corresponding to the energy of that state. The possibility of direct excitation by electrons in Rayleigh's apparatus is also suggested by the proximity of the anode to the region of excitation, since measurements taken in arcs have shown high electron temperatures near the anodes.[3]

The present investigation was undertaken to study in more detail the part played by these factors in the excitation of one vapor by the ionized vapor of a second metal. Ionized mercury distilled from an arc was used to excite sodium vapor, the vapors being mixed at a considerable distance from the arc so that the conditions were under control. Variations were

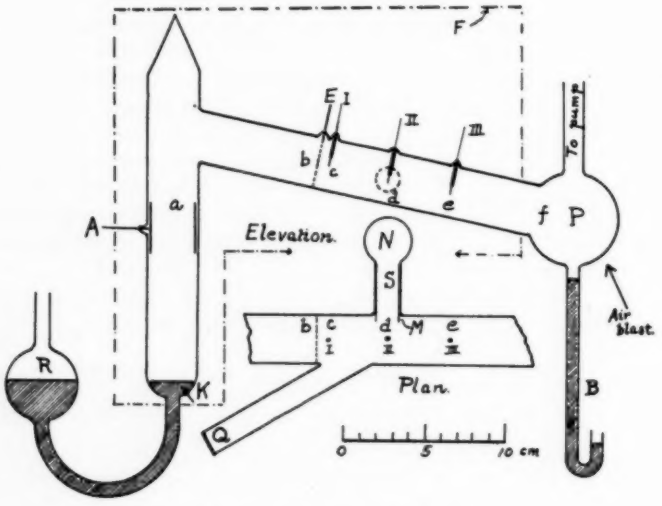

Fig. 1. Diagram of tube.

made in the concentration of mercury ions and excited $2^3P_{0,1}$ mercury atoms and the spectra resulting from each of these sources studied. Probes were used to measure the concentration of the ions and electrons and to determine the temperature of the latter.

Apparatus

The tube used is shown in Fig. 1, the essential parts drawn to scale. All parts were of Pyrex glass except the quartz observation window, Q, attached by a graded seal. The arc was between the mercury cathode, K, and the nickel cylindrical anode, A. The mercury evaporated by the arc and the heat from the surrounding furnace followed the path a, b, c, d, e, f, as a luminous stream to the air-cooled condenser, P, from which it was

[3] I. Langmuir and H. Mott-Smith, Jr., General Electric Rev. **27**, 449 (1924).

removed through the barometric column, *B*. Fresh pure mercury was supplied to the arc from a reservoir, *R*.

The sodium was introduced into the main tube and mixed with the streaming mercury vapor through the horizontal side tube, *S*, leading from the chamber *N*. To insure good mixing of the vapors and to avoid the creeping back of the sodium along the walls due to eddies, this side tube was extended several millimeters beyond the side wall by the nickel lining *M*. The disposition of the quartz observation window and of the sodium inlet tube was such as to prevent sodium from reaching the window and discoloring it. The rapid mercury vapor stream kept the sodium from diffusing up stream and only below *d* was discoloration of the walls due to sodium observed.

The dotted lines, *F*, indicate the oven which enclosed all parts of the mercury system except the reservoir *R* and the condensing system *P-B*. The heating elements were distributed so as to control the rate of evaporation and to prevent condensation of the mercury before reaching the condenser. The region *c-e* was superheated to prevent condensation of sodium. An independent heater surrounding *N* was used to control the sodium evaporation. The temperature of *N* was measured by a thermocouple.

The secondary electrode, *E*, called the "quenching electrode," filled the entire cross-section of the tube. It was of nickel gauze, the wires 0.3 mm diameter and 3 mm spacing. The probes I, II and III were of platinum wire, 0.025 mm diam., with an exposed length of 4 mm.

The tube was evacuated by a diffusion pump operating continuously during observations. Furthermore, the evaporating mercury made the tube itself a very effective diffusion pump.

The sodium, prepared by several distillations, was introduced directly into the chamber *N* or into a side chamber from which it was distilled into *N* in one or more steps to aid in eliminating the large amount of occluded gas. In spite of such precautions it was necessary to heat the sodium in *N* at a temperature just below that required to drive it into the main tube for some time before using, in order to reduce the gas emitted to such a point that it would no longer affect the results.

Observations at *d* were made with a quartz spectrograph through the window *Q*. Visual observations were possible through the glass walls at all points of the stream *a-e*.

Observations

The mercury vapor streaming from the arc contains many ions with an approximately equal number of electrons. The luminosity of this vapor, under the conditions of pressure used in these experiments, consisted so far as was observed only in the line spectrum of mercury.[4] This afterglow line spectrum depends upon the mercury ions and is usually ascribed to the excitation resulting from simple recombination. It differs from the ordinary

[4] Rayleigh, Proc. Roy. Soc. **A108,** 262 (1925); L. J. Hayner, Zeits. f. Physik **35,** 365 (1926).

arc spectrum in that the higher members of the different series are relatively more prominent in it. When sodium vapor was mixed with this luminous vapor the arc spectrum of sodium appeared, as described by Rayleigh, although with a different distribution of intensities.

Observations were made to distinguish between the spectrum of sodium produced by the excited mercury atoms, which term includes the metastable 2^3P_0 state and the closely associated 2^3P_1 state, (no evidence of the presence of the metastable 2^3P_2 state was found) and the spectrum of sodium produced by the mercury ions. We will understand by the latter all excitation of radiation by the ions, whether as the result of a direct transfer of the energy of ionization or as the result of recombination, in which process there may be formed excited atoms which later excite the sodium.

The distance from the arc, *a*, to the region of observation, *d-e*, was so great that, there remained in the streaming mercury vapor only a few of the many excited atoms formed in the arc. To study the spectrum produced by the excited atoms it was therefore necessary to introduce into the mercury stream a sufficient number of excited atoms to make their effect predominate over that of the ions. This was done by applying a small positive voltage (measured with respect to the anode) to the auxiliary or "quenching" electrode *E*, which considerably reduced (from 50 to 70 percent) the number of ions passing through *c-e*, and at the same time very greatly increased in that region the number of excited atoms. The ionic concentrations were measured by the probes, while the intensity of the line 2537 on the spectrograms was taken as a rough indicator of the concentration of the excited atoms.

The effect of a small positive voltage on *E* was to withdraw electrons from the stream (the current to *E* was several tenths of an ampere for 2.5 volts) and therefore to hold back a nearly equal number of positive ions in the region of the main arc. The increase in the average energy of the electrons due to the resulting voltage gradient in the region *b*, produced there new excitation without causing new ionization, provided the applied voltage was less than five volts. Consequently the stream of vapor carried down to the region *c-e* a large number of excited atoms. At the same time the partial withdrawal of the ions and electrons from this region resulted there in a very marked "quenching" of the mercury spectrum, with the exception of 2537. It will be convenient to refer to this condition of the tube as the "quenched" condition, the condition for *E* insulated being termed the "unquenched."

It was not possible to make use of negative voltages on *E*, although such also resulted in quenching of the mercury luminosity due to the withdrawal of positive ions by the electrode. The low mobility of these ions made it necessary to use large negative voltages to produce marked effect, and this resulted in direct excitation of the sodium, possibly as the result of oscillatory disturbances.

Visual observations of the sodium radiation with various amounts of sodium confirmed the above conclusions as to the conditions in the tube

with and without quenching. With a low sodium vapor pressure the unquenched condition gave very feeble excitation, while the application of the quenching voltage on E was accompanied by a marked increase of the whole sodium spectrum. This was the result of the higher probability of excitation by excited atoms than by ions. In both cases the excitation extended uniformly throughout *d-e*. As the sodium vapor pressure was increased the excitation by the excited atoms increased at first but finally reached a limit when the relatively small number of these atoms was used up in exciting the sodium. Furthermore, as the sodium pressure became greater the radiation due to the excited atoms became more and more concentrated toward the head of the sodium column, since the excited atoms were able to penetrate less deeply before meeting sodium atoms and losing their energy. On the other hand the excitation of sodium by the ions continued to increase with increase in the density of the sodium, and at very high vapor pressure surpassed the radiation due to the excited atoms. The excitation by the ions always remained nearly uniform throughout *d-e*, showing that there was not appreciable diminution of their number, which must therefore have been very large compared with the number of excited atoms produced by the voltage on E. Hence, with dense sodium the application of the quenching voltage produced the reverse of the result obtained with low pressure; the sodium radiation was markedly decreased since the quenching voltage decreased the number of ions, which were the predominant source of excitation.

Again, the individual lines of the sodium behaved differently. With only a slight increase of the density over the initial stage the lines 6161, 5896 and 5688 showed a decrease in intensity on applying the quenching voltage, while the lines 5154, 4752 and 4669 were still enhanced. These lines reversed in behaviour only when the vapor pressure became quite large. The significance of this will be seen later.

In the present experiments no direct excitation by the electrons was observed even though the electron temperature was greatly increased by the quenching process. The discussion of the temperature measurements will therefore be left to a later part of this paper.

Results

As shown above, with the tube in the quenched condition and with low sodium vapor density the sodium excitation was primarily by excited mercury atoms, while with the tube in the unquenched condition the sodium excitation was caused by the ions. Spectrograms were taken with the tube in each condition.

The results of microphotometric density measurements on typical spectrograms are tabulated in Table I. Column 1 gives the wave-lengths of all of the sodium lines found and of a few selected lines from the mercury spectrum. The sodium lines all occur as doublets, which were not resolved on the spectrograms. For brevity, each pair will be referred to in the table and in the following discussion by the longer wave-length component. Column 2

gives the corresponding series notation. Column 3 gives the excitation energy, expressed in wave-number units, required to bring the normal atom to the states necessary for the emission of the corresponding lines. Columns 4-8 record the photographic densities (Wratten and Wainwright Panchromatic plates.) Columns 4 and 6 are from spectrograms taken at *d* with the sodium

TABLE I. *Results of microphotometric measurements on typical spectrograms.*

1 Wave-lengths	2 Series Notation	3 Excitation energy	4 Unquenched condition	5 Quenched condition	6 Unquenched condition	7 Sodium arc	8 Mixed arc	9 $HgCl_2$ +Na
			Sodium					
11404	$2P-2S$	24738	*	*	*	*	*	
8195	$-3D$	29170	*	*	*	*	*	
6161	$-3S$	33199	0.04	0.03	0.02	1.70	0.13	trace
5896	$1S-2P$	16964	1.27	.63	1.32	2.40	large	100
5688	$2P-4D$	34547	.09	.05	.20	1.38	.48	1.0
5154	$-4S$	36371	.00	.04	.00	.26	.00	.15
4984	$-5D$	37033	.13	.20	.32	.41	.52	.30
4752	$-5S$	38010	.12	.67	.20	.07	1.12	.20
4669	$-6D$	38382	.16	.44	.30	.11	.43	.30
4546	$-6S$	38963	.00	.00	.00	.00	.00	.05
4500	$-7D$	39200	.21	.15	.23	trace	.13	.10
4424	$-7S$	39572	.00	.16	.00	.00	.00	.02
4394	$-8D$	39725	.00	.07	.00	.00	?	.05
3303	$1S-3P$	30269	.48	.51	.62	.00	.11	1.5
2853	$-4P$	35042	masked	.21	masked	†	†	.05
2680	$-5P$	37297	.02	.35	.04	†	†	.005
2594	$-6P$	38541	.00	.00	.00	†	†	.0005
			Mercury					
5461	$2^3P_2-2^3S_1$		0.06	.00	0.20		2.11	
4916	$2^1P_1-3^1S_0$		.37	.00	.67		1.30	
4358	$2^3P_1-2^3S_1$		.78	.00	1.10		large	
3663	$2^3P_2-3^3D_1$		.64	.00	1.05		large	weak
3341	$2^3P_2-3^3S_1$		.81	.00	.96		.32	
3131	$2^3P_1-3^3D_1$		.68	.00	.93		†	weak
2537	$1^1S_0-2^3P_1$	39413	.16	0.77	.24		†	1.0
Metastable atom	2^3P_0	37645						

* Plate not sensitive to these wave-lengths. † Not transmitted by walls.

excited by mercury with the tube in the unquenched condition. Column 5 is from a similar spectrogram with the tube in the quenched condition.

In column 7 are the results obtained with an arc in pure sodium vapor, given here for comparison as representing the "normal" sodium spectrum. This spectrum was taken with a cylindrical Pyrex tube 3.3 cm in diameter having a central hot cathode. The temperature of the tube was about 400°C. Columns 8 and 9 will be discussed later.

The conditions under which the spectrograms of columns 4 and 5 were taken were practically identical: arc current = 3.0 amps.; temperature of oven 235°C; column 4, *E* insulated, column 5, quenching voltage $E\text{-}A = 2.2$ volts; exposures 9 minutes. The concentration of the ions was approximately 7×10^{10} per cc when unquenched and 2.5×10^{10} per cc when quenched. The spectrogram of column 6 was taken under conditions best favoring the ex-

citation of sodium by mercury ions; E insulated, large arc current and large sodium density (N at 430°C). The exposure time was 10 minutes.

The photographic densities of the lines are given rather than the intensities, since with the data available the computation of the latter was quite inaccurate. It should be noted that the densities in general indicate a greater difference between a weak and a strong line than actually exists, and that furthermore the plate sensitivities are such that for equal densities lines in the region of 6161 are at least of ten-fold greater intensity than lines in the region of 4752.[5] In drawing conclusions we must confine comparisons of the densities to the individual line under different conditions and to immediately neighboring lines lying in a region of nearly constant plate characteristics.

It must also be remembered while studying these results that in all spectra the lower members of a series are by far the more easily excited. It is useful therefore, to look first at the ordinary sodium arc, which for purposes of comparison may be regarded as giving a normal intensity distribution. (See column 7) The densities of the lines decrease rapidly as we go to higher members of each series, and further the lines of the first subordinate series ($2P_{1/2,3/2}-mD$) are much stronger than the corresponding lines of the second subordinate series ($2P_{1/2,3/2}-mS$). We have 6161 much stronger than 5154 and 5154 stronger than 4752, with higher order terms too weak to be recorded. Again 4984 is stronger than 5154 and 4669 than 4752. If the actual intensities were given the decrease in intensity would be much more strongly marked. For this reason the density measurements are in the present case more convenient for studying the results than would be intensity measurements.

The excitation by excited atoms (column 5) gives a distribution of intensities quite different from that in the arc. It shows the marked "resonance" pointed out by Beutler and Josephy with maxima of excitation in the sodium spectrum corresponding to the energy of the metastable 2^3P_0 state of mercury (37645) and to the energy of the 2^3P_1 state (39413). The densities in the second subordinate series 6161, 5154, 4752, 4546, etc., increase to a maximum at 4752 and then decrease (4546 was observed faintly on one plate only). Similarly the first subordinate series 5688, 4984, 4669, 4500, etc., has a maximum at 4669, which is, however, less dense than 4752 although the first subordinate series is normally stronger than the second. As will be seen from column 3, 4752 corresponds most closely to the 2^3P_0 state as regards energy required to excite. There is a second, though less marked maximum between 4424 and 4394 corresponding closely to the energy available from the 2^3P_1 state. An examination of the principal series 5896, 3303, 2853, 2680, 2594, etc., shows, if we take into consideration the normal rapid decrease of intensity found as we go to higher members, a marked maximum at 2680 (energy 37297). This line is denser than 2853 and higher members were not found. This indicates marked excitation by the 2^3P_0 excited state, with the excitation in this series by the 2^3P_1 state too weak to record itself. Under the conditions of this experiment the excitation

[5] L. A. Jones and O. Sandvik, J.O.S.A. & R.S.I. **12**, 401. (1926).

by the metastable atom plays a much more important part than that by the 2^3P_1 atom.

The nature of the excitation by the mercury ions, when no appreciable number of primary excited atoms in the $2^3P_{0,1}$ states were present, is seen in columns 4 and 6. If we assume the excitation process to be a collision of a mercury atom with a neutral sodium atom, resulting in a sodium ion and either a normal or an excited mercury atom and followed by a recombination of the sodium ion with an electron, this spectrum should be the sodium "recombination spectrum." The higher members of the series should decrease less rapidly in intensity with respect to the lower members than in the normal arc, but if we may draw conclusions from the behavior of the mercury "recombination spectrum," we should still find a gradual decrease in intensity as we pass to higher members of each series. It will be seen that this was not the case, but that we have evidence again of a maximum near 4752. Note, for example in column 6 that 5154 has zero density while 4752 has density 0.20. 4752 is the only line of its series except 6161 found on the spectrograms. We may conclude that in the excitation of the sodium by the mercury ions there takes place both excitation due to the collision of the ions with sodium atoms and also considerable excitation by the metastable atoms which are formed as the result of the recombination of mercury ions and electrons. The degree to which this recombination was taking place is indicated by the strength of the mercury lines 4358 and 3131: note that these lines were not observable in the "quenched" spectrum (column 5). An alternative explanation of the excitation of sodium by ions will be discussed in the next to the last section of this paper.

A comparison of columns 4 and 5, which were from spectrograms taken under practically identical conditions except that in the first the number of ions was three times as great as in the second and there was a negligible number of primary excited atoms, shows that the lines 6161, 5896, and 5688, as compared with the group near 4752, are excited more easily by ions and less easily by the excited atoms. This explains the earlier observation that the application of a voltage to E quenches these lines at a much lower sodium pressure than the second group. Unfortunately, it is not possible completely to separate the spectra due to the two sources, since there were always a few ions producing excitation in the tube when in the quenched condition. However, this error was not large, and except for 5896, which is never simple in its behavior, owing to the fact that it always accompanies the emission of a subordinate series line and is highly affected by absorption, the spectrograms of columns 5 and 6 may be taken as typical of the two types of excitation.

Electron Temperatures

The three probes were used to study the ionization conditions at (I), a point between the "quenching electrode" and the sodium; (II), in the mixture of sodium and mercury vapors near the head of the mixed column: and (III), 4 cms below this point. The curves giving the relation between the logarithm of the electron current to a probe and the applied voltage

were used to determine the electron temperatures and the electron concentrations, as described by Langmuir and Mott-Smith.[3] The concentration of the positive ions was taken as approximately equal to that of the electrons.

The results of some of the concentration measurements have already been given. The electron temperature in the ionized mercury varied with the pressure conditions. The application of a quenching voltage on E increased this temperature by as much as three times, in one instance at probe I to 9000°. At this temperature it may be noted that 5% of the electrons would have a velocity corresponding to 2.1 volts or greater, sufficient to excite the D line, while one in 250 would have sufficient energy to excite the line 5688 and one in 600 to excite the line 4752. There was a marked lowering of electron temperature when the ionized mercury mixed with sodium vapor, as illustrated in Table II, which gives the electron temperatures at the three probes before and after sodium was introduced.

TABLE II. *Electron temperatures.*

Position of probe:	I	II	III
Mercury alone:	3050°K	2250°K	2400°K
Mercury and sodium:	2700	780	780

The temperature at I remained nearly constant since this probe was not in the sodium column. The temperatures at the other probes were decreased about 1500°.

In spite of these indications of a loss of electron energy due to the sodium, no definite evidence of direct excitation by electrons was obtained in these experiments. The changes in electron temperature could not be associated with changes in the sodium excitation, and furthermore with the tube in the quenched condition which gave the higher electron temperatures the spectrum was not such as would be expected from electron excitation. (Cf. columns 5 and 7, Table I) We conclude that under the conditions of this experiment direct electron excitation was negligible except possibly as accounting for some of the 5896 radiation.

In Rayleigh's experiment there is reason for expecting considerable excitation of the sodium by direct impact of electrons, because of the proximity of the anode. The fact that he found the principal series of sodium, when excited by mercury, only up to $m=3$ (2853) and lines in the first subordinate series only up to $m=4$ (4984), with no lines in the second subordinate series seems to indicate that electron excitation was the primary source of excitation. (Cf. column 7, Table I.) Since he did not report the finding of 4752 or 4669 we would conclude that no considerable excitation by excited atoms was present and that the excitation by ions was relatively small.

ENHANCEMENT OF MERCURY LINES

The behavior of the mercury lines in the region d was observed with different amounts of sodium introduced. The results of four exposures taken with E insulated are tabulated in Table III, which gives the densities of the more important mercury lines. The amount of sodium introduced is indicated by the temperature of N, but better by the densities of a few

sodium lines recorded in the table. In general no change in the strength of the mercury lines was observed which could not be accounted for by fluctuations of the arc, although the density of sodium was increased to the maximum possible with the apparatus. A remarkable enhancement was, however, observed in the five mercury lines 4916 ($2^1P_1-3^1S_0$), 2857 ($2^3P_0-3^1S_0$), 3341, 2894 and 2753 ($2^3P_{2,1,0}-3^3S_1$) all originating at the 3^1S_0 or 3^3S_1 levels. With N at 340°C the densities of these five lines are practically

TABLE III. *Behavior of mercury and sodium lines with varying amounts of sodium vapor present.*

Series Notation	Wave-length	Photographic densities for different temperatures at N 340°C	380°C	400°C	430°C
Mercury					
$2^3P_2-2^3S_1$	5461	0.07	0.08	0.08	0.20
$2^1P_1-3^1S_0$	4916	.00	.00	.06	.67
$2^3P_1-2^3S_1$	4358	.54	.79	.81	1.10
$2^3P_0-2^3S_1$	4047	.35	.34	.40	.60
$2^3P_2-3^3D_1$	3663	.98	.95	.97	1.05
$2^3P_2-3^3S_1$	3341	.03	.08	.46	.96
$2^3P_1-3^3D_1$	3131	.64	.97	.95	.93
$2^3P_1-3^3S_1$	2894	.06	.08	.38	.90
$2^3P_0-3^1S_0$	2857	.00	.00	.05	.48
$2^3P_0-3^3S_1$	2753	.00	.00	.15	.65
2^3P_2-6D	2699	.38	.42	.41	.34
$1^1S_0-2^3P_1$	2537	.26	.28	.27	.24
Sodium					
$1S-2P$	5896	0	0	.49	1.32
$2P-5D$	4984	0	0	weak	.32
$2P-5S$	4752	0	0	weak	.20
$1S-3P$	3303	0	weak	.17	.62

zero. As the temperature of N increases to 430°C, 4916 increases in density to 0.67, 3341 to 0.96 and the other three lines correspondingly. There is also some indication that the two lines 4916 and 2857 start to increase later than the other three.

It is difficult to explain the enhancement of these lines as due to two-body impacts. The energy available from an impact between a mercury ion and a sodium atom is too small for the excitation of the mercury to the 3^3S_1 level, which corresponds to 9.1 volts. Again the probability of the excitation of a sodium atom by a mercury ion and the subsequent excitation by the sodium of an excited mercury atom is very small, since the lives of the excited states in sodium are short and the concentration of excited mercury atoms low. It seems necessary to explain the result as due to three body impacts,[6] each involving a mercury ion, a normal sodium atom and an electron. It is noted that the energy necessary to excite a mercury atom already in the 2^3P_1 state to the 3^3S_1 state is 34549, expressed in wave-number units, and that the excitation energy of a sodium atom in the $4D$ state is

[6] Franck and Jordan, Anregung von Quantensprüngen durch Stösse, p. 183; M. Born and J. Franck, Zeits. f. Physik, **31**, 411 (1925); J. Franck, Zeits. f. Physik, **47**, 509 (1928).

very closely the same, 34547. Hence we assume the three body impact to result in a loosely bound molecule involving an excited mercury atom in the 2^3P_1 state and an excited sodium atom in the $4D$ state. The sodium atom then splits off after transferring its energy to the mercury atom which is left in the 3^3S_1 state. There is a much poorer correspondence between the energy difference, 34992, between the 2^3P_1 and 3^1S_0 levels, and the energy, 35040, of the nearest level of sodium, the $4P$ level.

If we accept the three body impact explanation we are led to consider the possibility that all of the excitation of the sodium by impact with mercury ions is the result of similar impacts. A comparison of the sum of the increases in the intensities of these five mercury lines as the result of addition of sodium, with the total radiation emitted simultaneously by the excited sodium shows that the number of impacts resulting in reexcitation of the mercury is of the same order of magnitude as the number resulting in sodium radiation. This suggests that all of the impacts between mercury ions and sodium atoms which result in radiation as observed in these experiments are of the same nature. If this is assumed it is probably not necessary to explain the marked excitation of 4752, when the tube was in the unquenched condition, as due to metastable atoms resulting from recombination.

It is interesting to note that the chemiluminescence spectrum of sodium produced by mixing sodium vapor and vaporized $HgCl_2$ is similar in some respects to the spectrum produced by ionized mercury. This spectrum as measured by Beutler, Bogdandi and Polanyi[7] is tabulated in column 9, Table I, the relative strength of the lines being expressed in units depending upon photographic densities. Comparing this column with column 6, we note that especially as regards the lines near 4752 the two spectra are quite similar. This fact would seem to fit in with the suggestion in regard to three body impacts made in the preceding paragraph. However, the presence of 2537 in the chemiluminescence spectrum suggests that the strong excitation of 4752 therein may result from the formation of metastable mercury atoms by the chemical reaction.

The drop in the electron temperature in the mercury stream caused by the sodium, was expected to result in an increase in the rate of recombination of the mercury ions, and consequently in an increase in the intensity of all the mercury lines.[8] The results did not give the expected increase. However, there is some doubt as to the significance of this.

Arcs in Mixed Vapors

The above results were compared with the spectra from an arc in a mixture of mercury and sodium vapor. The arc was in the tube with hot cathode already described in connection with column 7, Table I. The metals were introduced as an amalgam and the temperature was such as to give mercury and sodium lines of about equal intensity. The radiation was

[7] Beutler, Bogdandi and Polanyi, Naturwiss. **14,** 164 (1926).

[8] L. J. Hayner, reference 4, p. 380; F. L. Mohler, Phys. Rev. **31,** 187 (1928); Carl Kenty, Phys. Rev. **32,** 624, (1928).

taken from near the cathode. The results for the sodium lines as measured roughly from one plate, are recorded in column 8, Table I. A comparison of these densities with those in columns 4-7 leads to the conclusion that, except for 5896 (too dense to measure on the plate) which is probably excited in large part by electron impact, the sodium lines owe their excitation almost entirely to the ionized or to the excited mercury atoms. Because of its much greater vapor pressure the mercury was responsible for practically all of the primary excitation. The large part played by the excitation by metastable atoms is indicated by the strength of 4752.

The mercury lines 4916 and 3341, are greatly enhanced in this arc, as compared with the same lines in an arc in pure mercury photographed in the same tube, in confirmation of the results already described. 2894, 2857 and 2753 were not transmitted by the glass.

Spark Line 3984

Rayleigh[9] has called attention to the absence of the mercury spark line 3984 in the luminous vapor distilled from the arc. This line was found during these experiments in the mercury column *d-e*, in one instance. The electrode *E* was insulated and a small amount of sodium was being introduced into the luminous mercury. The exposure time was two hours. It is not certain whether the appearance of the line was due to the sodium vapor, to the long exposure or to other causes. The line was not found on any of the other plates.

In conclusion we wish to express our thanks to Mr. R. C. Garth and Mr. George Dean for their assistance in carrying out these experiments.

Physics Laboratories,
Columbia University.
December, 1928.

[9] Rayleigh, Proc. Roy. Soc. **A108**, 262 (1925).

THE ZEEMAN EFFECT IN THE ANGSTROM CO BANDS. II

By F. H. Crawford

Abstract

This paper is a continuation of the work previously reported in this Journal (Phys. Rev. **30**, 438 (1927)). *Experimental Improvements.* The former source for the CO spectrum has been replaced by a Pyrex *discharge tube* placed longitudinally in the field. By special construction and the use of a forced-draft cooling system it has been possible to increase the intensity of the source about fourfold and to eliminate impurity bands previously the source of much trouble. *Field strengths* were determined from the Zeeman triplet (five-halves normal) of the W λ4660 line. This pattern could be obtained with great sharpness from a brass-tungsten intermittent arc operating in the open air and was standardized against Zn lines in vacuo. Its magnitude between 15000 and 28000 gauss was proportional to the field within ±0.4 percent. The Hg lines λ4047 and 4358 were used as field standards in later parts of the work. *Results.* Observations of the Zeeman effect have been extended from the bands at λλ5610, 5198 and 4835 to include λλ4511 and 4394. Measurements on thirty patterns with M (the ordinal number of the line in a branch) = 1, for fields from 18000 to 36000 gauss, have shown the widths of the Zeeman patterns to be proportional to the field strengths to within 2 percent, the estimated accuracy of measurement. The weighted average of the pattern widths for $M=1$ is 97.7 percent $\Delta\nu_n$ and $M=2$, 66.3 percent $\Delta\nu_n$, where $\Delta\nu_n$ is the normal Lorentz triplet half-width. The quantum mechanics predicts 100 percent $\Delta\nu_n$ and 66.7 percent $\Delta\nu_n$ for these widths respectively as against 88.9 percent and 64 percent on the old quantum theory. Thirteen out of the possible eighteen patterns predicted for the first two lines of the P, Q, and R branches have been resolved and measured and found to agree with predictions within the error of measurement. The intensity asymmetries reported previously and later treated theoretically by Kronig (Phys. Rev. **31**, 195 (1928)) have been found wherever comparison in both high and low fields was possible to behave qualitatively (though *not quantitatively*) as Kronig's calculations predict. Eight isolated lines ($M=23$ to $M=35$) in four bands have been found which show anomalously large Zeeman effects. Three (and possibly four) new bands have been observed which from their behavior in the magnetic field must belong to the Angstrom group. Their analysis is reserved for another paper.

I. General

IN A previous paper[1] a theoretical account of and experimental results for the Zeeman effect in three of the Angstrom bands of carbon-monoxide are given. As was there pointed out the qualitative features of the Zeeman effect in band lines as predicted by the conventional quantum theory[2] and the quantum mechanics[3] are the same. Each predicts that the Zeeman pattern for electronic transitions of the type $^1S \rightarrow {}^1P$ (to which type these

[1] E. C. Kemble, R. S. Mulliken and F. H. Crawford, Phys. Rev. **30**, 438 (1928). This will hereafter be referred to as Part I.

[2] E. C. Kemble, Phys. Rev. **27**, 799A (1926); "Molecular Spectra in Gases," National Research Council Bulletin 57, Chap. VII; H. A. Karmers and W. Pauli, Jr., Zeits. f. Physik **13**, 35 (1923).

[3] J. H. Van Vleck, Phys. Rev. **28**, 980 (1926); D. M. Dennison, Phys. Rev. **28**, 318 (1926).

bands belong[4]) will be symmetrical about the position of the original line, will be of the same magnitude for corresponding lines in different branches and will be of the greatest magnitude for the first line in a branch. The patterns will then decrease uniformly in size with the serial number M of the line in the branch, the number of components in each pattern being $(2M+1)$. As a matter of fact the total pattern-width, $\Delta\nu$, in cm^{-1} is

$$\Delta\nu=\frac{2}{(M+1+1/4M)}\cdot\Delta\nu_n \tag{1}$$

on the old theory, and

$$\Delta\nu=\frac{2}{(M+1)}\Delta\nu_n \tag{2}$$

on the quantum mechanics.[4a] Here as before $\Delta\nu_n$ is the half-width of the normal Zeeman triplet. From these it appears that the predictions for $M>2$ differ by one percent or less and hence are incapable of experimental differentiation. For $M=1$ the results, however, differ by 11.1 percent and for $M=2$ by 2.7 percent. Consequently although there is no doubt about the fundamentally greater soundness of the quantum-mechanics treatment it seemed highly desirable to discover which was in closer agreement with experimental facts. In Part I the small number of good plates available gave average values falling midway between the two predictions. The results of recent measurements on some thirty Zeeman patterns of lines with $M=1$ fall distinctly nearer the value calculated from (2) [as do those for $M=2$, though the number of trustworthy measurements for the latter case is only 3.]

In Part I likewise theoretical *intensities*[5] of the components in the Zeeman patterns were given and were found to agree in general with the visually estimated intensities in the resolved patterns and with the general size and appearance of the patterns for the higher lines where complete resolution was not possible. There remained nevertheless certain small but distinct departures from the theoretical intensities for the P and Q line patterns (see Part I, page 453) which were later shown by Kronig[6] to be due to the perturbing action of the high magnetic fields. The very satisfactory agreement of the predicted perturbations with the observed intensities and the

[4] R. S. Mulliken, Phys. Rev. **28**, 482 (1926).

[4a] Eqs. (1) and (2) here correspond to Eqs. (6) and (7) in Part I (page 443). Unfortunately Eq. (6) is incorrectly printed both there and in Fig. 6 (page 455). The quantity to be added to $(M+1)$ in the denominator of Eq. (6) is $1/4M$ and *not* $M/4$.

[5] The intensity of the components in a Zeeman pattern were found by combining the formulas deduced for line spectra from the summation rule by Kronig [R. deL. Kronig, Zeits. f. Physik **31**, 885 (1925)] and Hönl [H. Hönl, Zeits. f. Physik **31**, 340 (1925)] with those deduced by Hönl and London [H. Hönl and F. London, Naturwiss. **13**, 756 (1925); Zeits. f. Physik **33**, 803 (1925)] for the relative intensities of the unperturbed lines. These combination formulas are in harmony with those obtained by Dennison (see footnote 3) from the matrix mechanics. Obviously these formulas are strictly valid only for small fields as Kronig later showed (footnote 6).

[6] R. deL. Kronig, Phys. Rev. **31**, 195 (1928).

disappearance of the effect at lower fields will be discussed in detail in the sequel.

The interpretation of the photographs on which the conclusions of Part I are based was in many cases rendered difficult by the faintness of the early lines and the presence of a faint background of impurity lines. Due to the lengths of exposure required (15 to 40 hours) a no-field comparison photograph was taken with only one set of plates. Consequently the positive interpretation of the results necessitated very minute examination and careful comparison of all of the plates. Every line appearing near the head of each band was measured on every available plate, the intensity of each line being estimated visually, and the results thus collected were compared with the data from the no-field exposure. By this laborious process it was possible to distinguish impurity lines from Zeeman effect components by the fact that they were either (1) not present regularly on all of the plates, or (2) were characteristically different in physical appearance from Zeeman components about which there was no doubt, or (3) showed at most only a broadening in the field with no relative displacement in different fields. Results obtained from later photographs, where, due to greater intensity, entirely different modes of excitation, and elimination of many impurity lines (bands!) these sources of ambiguity have been pretty largely removed, have not in any case been in disagreement with the conclusions arrived at in Part I.

The general questions which earlier work left unsettled or in a state such that more evidence was desirable were the following: 1 The proportionality of pattern-width to field strength, 2 The nature of the patterns for the lines $R(1)$, $R(2)$, and $Q(2)$, 3 The behavior of the perturbed intensities with different fields and 4 The nature and occurence of the anomalously large Zeeman patterns in higher lines ($M > 23$ usually). In addition it was hoped to extend the observations to the other strong bands (λλ4511, 4394 and 4123) of the Angstrom group where previously impurities had rendered observation quite impossible.

II. Experimental Details and Improvements

For all of these questions greater intensity and the elimination of as many impurity lines as possible were seen to be quite necessary. Since 30-hour exposures with the Back vacuum box[7] gave only the first order with usable intensity, it seemed inadvisable by prolonging the time to obtain a higher order photograph (quite aside from the physical strain of tending the apparatus over such protracted intervals, unavoidable temperature fluctuations—due to sudden changes in the weather—and the cumulative effect of small jars and vibrations in the building seemed to place a practical limit on the length of exposure.). Actually a 45-hour run with the Back box gave poorer results than some of the shorter ones. Hence it was decided that other methods must be devised which would be more suitable for exciting

[7] See Part I, page 445.

gaseous molecular spectra than the Back box with high-tension electrodes. (This type of source was designed primarily for exciting metallic lines and for such is probably unequalled. For gaseous spectra, however, the discharge spreads through too great a volume to be very brilliant.).

Giving up the Back box necessitated two things—first, a new source where the discharge was sufficiently confined to give greater intensity than before and second, another method of determining the field strength.

Excitation of the CO spectrum. The requirements for the new source were two and these were mutually somewhat conflicting. It was necessary to obtain a great increase in photographic intensity and at the same time effect a reduction in the undesired band spectra excited. The attainment of the first requirement was limited in practise by the necessity of keeping down the mean effective temperature in the discharge since high temperatures favor the production of the lines of high rotational quantum number (j''-value)[8] as against the earlier lines in the branch.[9] The attainment of the second requirement was limited by the practicable limits of chemical purification of the carbon-dioxide and the appearance after long exposures

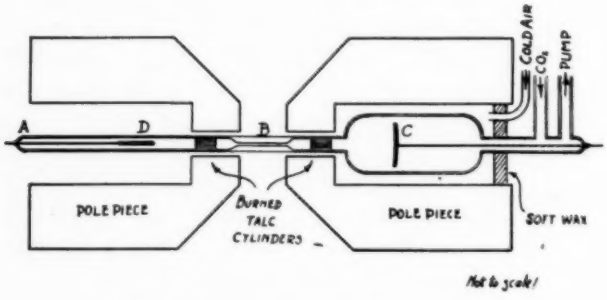

Fig. 1. Discharge tube in magnet.

of a background of very fine lines. These extended from the mass of ultraviolet bands of Deslandres and d'Azambuya to the limits of photographic sensitivity of the plates in the red. The enormous number and closeness of the lines, (often 10 or 15 per Angstrom) together with no very obvious structural regularities suggest that the CO_2 molecule is possibly the origin. Attempts to test this by using CO for the discharge rather than CO_2 were not decisive.

Several types of discharge tubes were tried including quartz tubes having the capillary perpendicular to the field. In all cases the heavy current required soon ruptured the walls or at least rendered them quite opaque. Consequently a Pyrex tube placed along the axis of the magnet was eventually resorted to. A great number of various designs were used of which that in Fig. 1 was the most successful. This figure shows the tube in place in the magnet.

[8] In these bands the M-value of the line and the final rotational quantum number, j'' (in the quantum mechanics) are the same.

[9] See R. S. Mulliken, Phys. Rev. **29**, 411 (1927).

The following points regarding the design and operation of the tube are to be noted:

1. The seals for the electrode are placed as far from the discharge end of the electrode as possible (10 to 15 cm is usually sufficient). This prevents the softening of the seal and development of slow leaks.[10] 2. Use of fine capillary at *B* (Fig. 2). Thermometer capillary of internal bore 0.3 to 0.5 mm gave the most brilliant discharge. 3. Use of massive tungsten electrode at *C* having large surface area. This minimized the oxidation so troublesome when a single heavy wire was used. The oxide so formed diffused slowly down the tube and deposited in the capillary rendering its walls fairly opaque after a few hours operation. 4. Placing perforated cylinders of talc on either side of capillary to catch small amounts of oxide diffusing from electrode. These cylinders of talc were bored longitudinally with 8 or 10 half millimeter holes and baked at 950°C for 5 hours or so before being placed in the discharge tube. They acted as effective traps for the tungsten oxide without increasing too greatly the resistance of the tube to the discharge. The tube could be run continuously for 40 hours before it was necessary to cut out the capillary and replace it with a fresh one.[11] 5. Cooling of tube by air blast. When the maximum discharge from a half kilowatt transformer was sent through the tube—confined in its small hole in the magnet—the glass usually softened at some point or other in 10 or 15 minutes. When, however, a blast of cool air was blown continuously through the annular space around the tube this was entirely prevented.

This source is at least 4 times as intense photographically as the one described in Part I (page 445), requires less attention during operation and gives a spectrum almost entirely free from N_2 bands (minute leaks in the Back box made it difficult to keep small amounts of air out of the discharge). Of course, since the capillary was horizontal and the slit of the grating vertical it was necessary to rotate the image of the former through 90°. This was accomplished in the well-known way by using a large-faced 45° prism between the focussing lens and the slit, the plane of the largest face being parallel to the optic axis of the lens, the 90°-edge of the prism lying in a vertical plane and making an angle of 45° with the slit of the grating.

Field-strength determinations. The monumental work of Bàck and Landé of the Zeeman effect in line spectra necessitated, of course, the development of a method and technique for measuring fields of all sizes with high precision. All requirements seemed to be met by the vacuum arc between wobbling zinc electrodes developed by them[12] and used previously by us (cf Part I, 447). There appeared, however, to be no obvious way of adapting such a vacuum metallic arc to the magnet set up for use with a glass discharge tube.

[10] It is quite necessary to prevent all access of air since the nitrogen band spectrum is excited so strongly in this type of tube that in 5 minutes it can ruin a 24-hour CO photograph.

[11] This was very important since it was quite necessary not to disturb the optical system until both the exposure without field (10 hours or so) and that with field (25 to 30 hours) had been completed.

[12] Cf. Back and Landé, Zeemaneffekt u. Multiplettstruktur, page 124.

Preliminary experiments with a self-interrupting arc[13]—see Fig. 2—showed that this would be suitable at least for high fields. The device is placed between the poles of the electromagnet and a current of 3 to 8 amperes sent through in such a direction that the ponderomotive force acting on the arm A causes it to turn (upward) on a pivot at O, thus drawing the current out into a momentary arc at B. The weight of A then causes it to drop, and the process is repeated. In order to obtain the zinc triplet (λλ4680, 4722, 4810) with sufficient intensity, it is necessary to connect a capacity (5 to 20 microfarads) across the gap. But under these circumstances the lines are diffuse and quite unsuited for accurate measurement. If now a large inductance (10 to 30 millihenrys) is connected in series with the capacity, the lines are greatly sharpened.[14] By varying current, capacity inductance and frequency of interruption (by adjusting the counterpoise C—Fig. 2) the lines could be obtained sufficiently sharply for the field to be determined to less than a percent (from second order photographs). This method was not, however, entirely satisfactory, due to the rapid burning away of the brass with the consequent forming of a crater of oxide on the lower electrode. After the arc had run for 10 minutes, the lines were much less sharp than when first started.

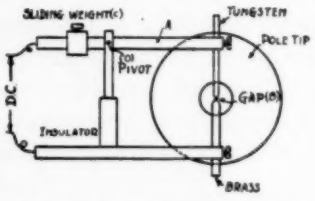

Fig. 2. Self-interrupting arc.

Fortunately there always appeared on the zinc plates an extremely sharp Zeeman triplet, identified as that of the tungsten line at λ4660. The components of this triplet are as sharp as those obtained from a zinc arc in vacuo and in addition, the total width of the triplet is $5\Delta\nu_n$. The accurate proportionality of the pattern of the tungsten line was proved by standardization against zinc patterns in vacuo and held within less than ± 0.4 percent for fields between 15,000 and 28,000 gauss. In later parts of the work a special discharge tube for mercury was made and the patterns of the lines of the spectroscopic triplet λλ4047, 4358 and 5461 were used.[15] The first two lines were obtained in both first and second orders of the grating in a 5 minute exposure and gave values for the field differing from one another by not over 0.3 percent.

III. Results

1. Proportionality of pattern width to field strength. Since the general simplicity and regularity of the CO Angstrom bands gives every reason for supposing that the molecule is very rigid, it appeared desirable to show that the consequent predicted linearity of the Zeeman effect with field was actually observed. In Part I this approximate linearity was established from measurements on the $P(1)$ and $Q(1)$ patterns of λ5610 and λ5198 at fields

[13] Due in principle to Professor H. Crew.

[14] C. R. Helmsalech, **152,** 1007 (1911); **152** 1086 (1911); and many others before and since.

[15] See Gmelin, Ann. d. Physik **29,** 1079 et seq. (1909); Runge and Paschen, Ann. d. Physik (IV) **39,** 897 (1912).

of 36,000 and 25,000 (5 individual measurements). In the course of investigating the other bands of the series, data have been obtained on fields of 28,000 and 19,000 to 21,000 from five different bands and a dozen or so different plates, (all told some 30 individual measurements). These data together with those previously obtained are summarized in Table I where

TABLE I.

Band	Line	Plates used	$\Delta\nu$ observed (cm^{-1})	Average field (gauss)	$\Delta\nu_n$ (cm^{-1})	$\frac{\Delta\nu}{\Delta\nu_n}$ (percent)
λ5610	Q(1)	5	0.887	19,670	0.924	96.0
	Q̃(1)	1	1.088	24,400	1.147	94.8
	Q̃(1)	1	1.272	28,050	1.319	96.5
	Q̃(1)	2	1.546	34,900	1.641	94.2
	P̃(1)	2	.916	19,880	.934	98.1
	P(1)	1	1.104	24,400	1.147	96.1
	P(1)	1	1.300	28,050	1.319	98.5
	Q(2)	2	.616	19,650	.923	66.7
	Q̃(2)	1	.853	28,050		64.7
5198	Q(1)	4	.902	19,950	.937	96.2
	Q̃(1)	1	1.084	24,400	1.147	94.4
	Q̃(1)	1	1.287	28,050		97.5
4035	Q(1)	3	(.76)	19,300	.907	(84) ±10
4511	Q(1)	4	.919	19,780	.929	97.9
	P̃(1)	2	.962	19,690	.925	104
	R(1)	3	.939	19,800	.930	101
4394	Q(1)	2	.79	19,300	.907	87

the total pattern widths are expressed in percent of $\Delta\nu_n$ as well as in inverse cm for the field in question. In Fig. 3 these pattern widths (expressed in cm^{-1}) are plotted against field strength for $M=1$ and $M=2$. In both cases the upper and lower straight lines represent the predictions respectively of Eq. (2) and (1). While the observed points fall in general somewhat below the upper curve they certainly lie closer to it than to the lower one. In fact the weighted average (weighted only according to actual size of pattern being measured on plate) of all determinations[16], for $M=1$ (expressed in percent of $\Delta\nu_n$) is 97.7 percent (±2. percent) and for $M=2$, 66.3 percent (±1.4 percent). Eq. (2) and (1) give for $M=1$, 100 percent and 88.9 percent respectively and for $M=2$, 66.7 percent and 64.0 percent respectively. Hence the experimental results are described more satisfactorily by the quantum mechanics (i.e. by Eq. (2) of this paper).[16a]

[16] I have not included in this average the values from the band λ4835. The grating did not seem to be so accurately in focus for this region in the II order. The combination of faintness and lack of focus rendered quantitative measurements untrustworthy.

[16a] It should be pointed out that on the quantum mechanics high fields produce a *second order* perturbation in the energy levels (and hence pattern widths) which is associated with a *first order* perturbation in the transition probabilities (and hence intensities of components). The latter effect is that calculated by Kronig and found to agree qualitatively with observation. It is possible that the tendency for the patterns for $M=1$ to depart more from 100

2. Nature of patterns for lines R(1), R(2) and Q(2). As a result of the increased intensity and reduction of impurities it has been possible to resolve and measure 13 out of the possible 18 characteristic patterns predicted for the six lines, $P(1)$, $Q(1)$, $R(1)$, $P(2)$, $Q(2)$ and $R(2)$ [counting no polarization, parallel polarization and perpendicular polarization as 3 separate cases (see Fig. 1, Part I, page 444).] The other five patterns, viz. $\sigma \cdot \pi R(2)$, $\sigma \cdot R(2)$, $\pi \cdot R(2)$, $\sigma \cdot Q(2)$ and $\sigma \cdot \pi P(2)$, had in each case the calculated over-all width and the expected intensity distribution. (Here as before σ refers to the part

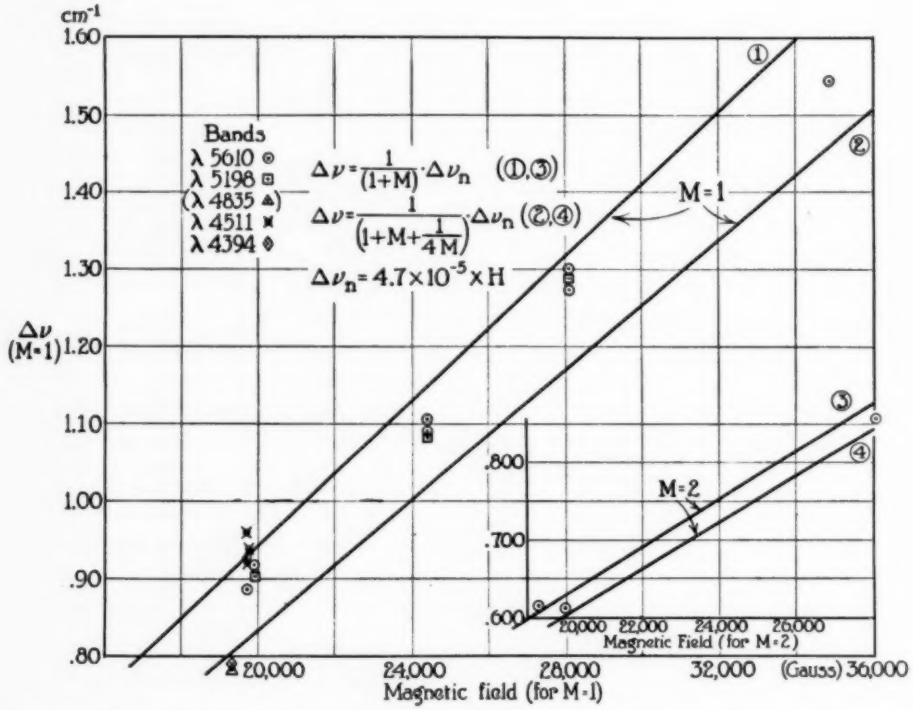

Fig. 3. The observed widths of Zeeman patterns (in cm^{-1}) are plotted against field strength for the cases of $M=1$ and $M=2$ from the data of Table I. Most of the points represent the average of measurements on from two to five different plates. The measurements for $M=2$ were made only on patterns actually resolved and represented the widths between the extreme components of the quintette patterns. In general the measurements on the Q lines of λ5610 are the most trustworthy.

of the pattern observed in perpendicular polarization, π that observed in parallel polarization and $\sigma \cdot \pi$ when no polarizing prism was used.) In particular the $\sigma \cdot \pi R(2)$ patterns were uniformly broad bands showing *no* tendency

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percent $\Delta\nu_n$ at *high fields* than at low fields is due to the existence of this second order effect. Two accurate measurements on $Q(1)$ at $H=35{,}000$ give a width of 94.2 percent $\Delta\nu_n$ against 98 percent for the patterns measured around 20,000 gauss. Many more measurements at the high field, however, would be required before this could be taken as definitely ascertained.

to lightness in the center as previously reported from one plate. This has been confirmed on four plates.

The $R(1)$ pattern has been obtained on four (and possible five) plates and as was expected had the same general appearance in both polarizations.

The resolution of the $Q(2)$ line into its quintette patterns was definitely obtained on two recent plates (λ5610 band). On the λ5610 plate on which this pattern was previously found to be resolved the intensity was so small that there was always the bare possibility that the line identified as the $\pi Q(2)_{+1}$ component might have been simply part of the very faint fringe usually found near the edge of a strong line (in this case $P(9)$, a line about 15 times as intense as the above Zeeman component). Resolution of the pattern for both parallel polarization and no polarization definitely removes this doubt (particularly when taken along with the quantitative agreement of the size of the pattern with the prediction for the lower field).

The higher lines ($M>2$) have been re-examined and as previously reported confirm all details of the theory. In particular the "Q-doublets" (parallel polarization) on second order photographs have been traced as far as $Q(14)$ for λ5610, $Q(11)$ for λ5194, $Q(10)$ for λ4835 and $Q(11)$ for λ4511.

3. Intensity perturbations for Zeeman components. In Part I the fact that the "Q-doublets" (parallel polarization) and presumably[17] the "P-doublets" (perpendicular polarization) were unsymmetrical in intensity was particularly emphasized. According to the simple theory, the intensities as well as the displacements should be symmetrical in parallel and perpendicular polarization whereas actually in parallel polarization the components of the Q patterns are more intense on the low-frequency side (i.e. on the side towards the band head). Recently Kronig[18] has shown on the basis of the quantum mechanics that this is precisely what is to be expected at high fields and that the intensity relations contained in Eqs. 8A to 10B inclusive (Part I, page 444) are in reality strictly true only for the limiting case of zero field strength. Kronig calculates the perturbative effect of the field on the normal transition probabilities for transitions from the upper magnetically insensitive state, ^1S, to the lower magnetically subdivided state, ^1P. He finds to a first approximation that the relative changes in the normal intensities (i.e., those calculated for the limiting case of $H=0$) are directly proportional to the field strength and are of such a nature that the decrease in intensity for a given Zeeman component on one side of the undisplaced line is added to the original intensity of the symmetrically situated component on the other side of the line. Thus, if j[19] and r are final rotational and magnetic quantum numbers respectively and I' and I'' are moments of inertia characteristic of the ^1S and ^1P, electronic states of the molecule, the expression giving the *relative change* in the intensity of a Zeeman component

[17] Only $P(1)$ could be observed due to the presence of so many other lines.

[18] R. de L. Kronig, Phys. Rev. **31**, 195 (1928).

[19] This is a rotational quantum number in the new mechanics and for the case in hand is $\frac{1}{2}$ unit lower than those in which the formulas of Part I are expressed.

of a line of the Q branch (for which ordinal number, M, of line is numerically equal to the value of j) in parallel polarization is:

$$\epsilon_z(l'jr\ ;\ l''jr)=\frac{8\pi^2\mu_1 I''H}{h^2}\ \frac{(j^2-1)(j^2-r^2)}{j^2(2j-1)(2j+1)r}+\frac{j(j+2)[(j+1)^2-r^2]}{(j+1)^2(2j+1)(2j+3)r} \qquad (3)$$

(Here the subscript z refers to the direction of the magnetic field, H.) In this expression μ_1 is the value of the Bohr magneton $eh/m4\pi$. The coefficient can conveniently be written as $K\Delta\nu_n$, where $\Delta\nu_n$ is the normal Zeeman half-width for field H and K is 0.635. Now we see that for negative r's the expression is negative, and for positive r's, positive.[20] In other words, the low-frequency components have their relative intensities increased, while the high-frequency ones have theirs decreased. Moreover, as j gets larger and larger, the effect tends to vanish.

The expression for the P branch in parallel polarization is:

$$\epsilon_z(l'jr\ ;\ l_1''j+1r)=-\frac{8\pi^2\mu_1 I''H}{h^2}\ \frac{r}{(j+1)^2} \qquad (4)$$

where the transition to negative r's refers as before to the components on the low-frequency side of the pattern. But here ϵ is negative, so the intensity *decreases*. Hence the behavior of the P patterns should be opposite that of the "Q-doublets." As a matter of fact, the two effects are not just the reverse of one another, since the relative weakening of the P components is greater than for the Q components except for the first line in the branch. In Fig. 4 I have drawn the theoretical Zeeman intensity patterns for the first two lines of the P and Q branches for perturbing fields of $H=0$ (when the intensities are symmetrical), of $H=20{,}000$ and of $H=35{,}000$ gauss, using Eqs. (3) and (4) and the others given by Kronig. [For convenience all of the pattern *widths* are drawn to the same scale (otherwise the pattern for $H=0$ would have zero width).] The values of the field given in Fig. 4 are the ones used in computing the perturbed intensities.]

A detailed comparison with the plates has shown that the intensities behave in general as expected, the asymmetries becoming less for small fields. In all cases, of course, the effects are small changes in the intensities of already weak lines and consequently too much cannot be expected from a visual observation. In the case of the R lines the predicted effect is small even for high fields. Since R lines were resolved only for low fields any lack of symmetry would be still smaller and hence beyond observation.

P lines. For the $P(1)$ line no effect is predicted for *either* polarization. Actually the low frequency component seems to be less intense than the high frequency one on several plates (λ5610) both at $H=20{,}000$ and $H=24{,}400$ gauss. This result is probably not a real contradiction with theory

[20] In Part I the opposite convention was used, i.e., positive r's corresponded to high frequency components and negative r's to low frequency components. No confusion need arise if intensities are computed properly from Kronig's expression and diagrams labeled in terms of *our* notation.

but is to be assigned to "weakening" [due to the immediate proximity of the strong line $P(7)$] of the low frequency component in development since in λ5198 where both components are equally distant from a strong line no such lack of symmetry is observed even for $H=35{,}000$ gauss. For the $P(2)$ line in parallel polarization the theory predicts that at $H=35{,}000$ the low frequency member of the narrow triplet (see Figs. 4 and 5) should be only about one half the intensity of the other two components of the pattern. This accounts in part at least for its non-appearance in the reproduction of Fig. 5. At lower fields while the pattern was not resolved it was at least

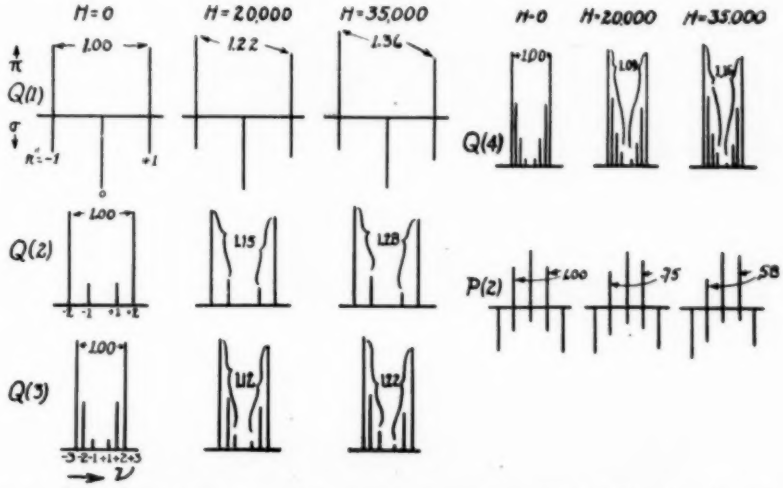

Fig. 4. Theoretical intensities of Zeeman patterns according to Kronig. Here the intensities are plotted for perturbing fields of 0, 20,000 and 35,000 gauss (where for convenience the pattern *widths* for a given M value are drawn to the same scale) for lines $Q(1)$, $Q(2)$, $Q(3)$, $Q(4)$ and $P(2)$. Components polarized $\parallel$ (π) to the field are drawn upward and those polarized perpendicularly (σ) are drawn downward. The number written in each pattern is the ratio of the sums of the intensities of the low frequency components to the sum of the intensities of the high frequency components for that pattern. Where the individual components thus added are too close together to be resolved on the photograph these ratios are approximately the intensity ratios for the observed doublet-like pattern.

more nearly symmetrical about the undisplaced position of the original line.[20a]

Q lines. In the case of the Q lines observation is easier and the qualitative results more satisfactory. In parallel polarization theory predicts greater intensity for the low frequency components. The asymmetry should be greatest for $M=1$ and decrease gradually for larger M. At $H=35{,}000$ both members of the $Q(1)$ doublet can be observed in only one band. In this case the high frequency component is undoubtedly weaker though this may be in large part caused by the immediate nearness of the strong line $P(9)$. The asymmetry gradually decreases however with M and is not observable for

[20a] In perpendicular polarization the $P(2)$ pattern has its low frequency edge too close to the (now broad) pattern of the $P(6)$ line to be clearly resolved from it.

$M>7$. At $H=20{,}000$ it is very small for $Q(1)$ and cannot be detected (visually) beyond $M=3$ or 4. In perpendicular polarization the unresolved lines are mere broad bands for $M>2$. For $M=1$ the outside components are too faint to show in the weak high-field photographs while at $H=20{,}000$ the pattern is practically symmetrical. The theory thus predicts no effects which are not *qualitatively* in close agreement with observations. As to the quantitative results, however, the theory seems to predict that the asymmetry should increase rather more slowly with field than it actually does. Thus for the highest fields (35,000) if we take the case of $\pi \cdot Q(3)$ and simply

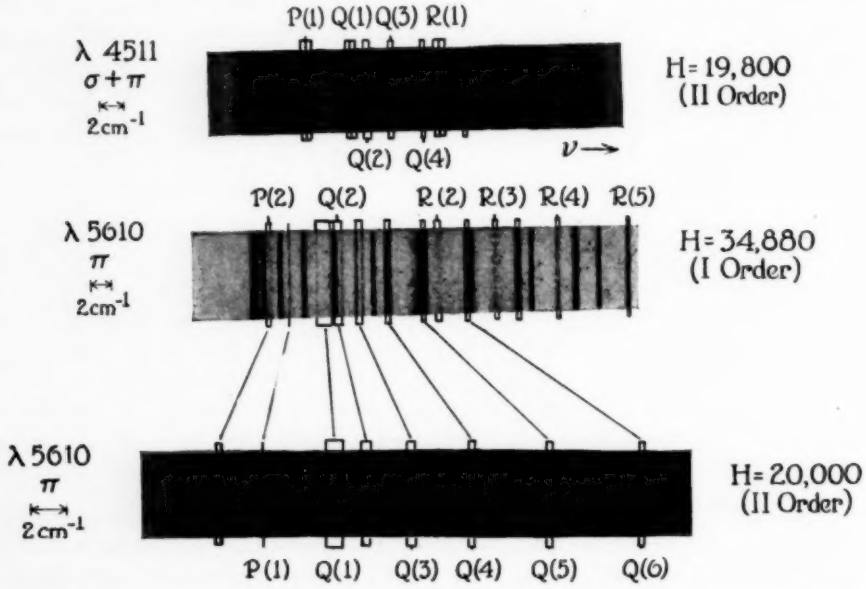

Fig. 5. The upper photograph shows an enlargement (from a second order plate) of the head of the λ4511 band showing in particular the two high frequency components of the $P(1)$ triplets and the very faint $R(1)$ triplet. In the second photograph is a portion of the λ5610 band (first order plate and $\|$ polarization). Here the asymmetry of the Q-"doublets" [particularly $Q(3)$ and $Q(4)$] is to be noted and compared with the near symmetry in the lower photograph which represents the same band in $\|$ polarization at a *lower field*. At $H=34{,}880$ gauss the two high frequency components only of the $\pi \cdot P(2)$ patterns are visible. At the lower field the pattern is not resolved but on the plate looks too wide to be the unresolved pattern of less than three components (compare with the theoretical patterns in Fig. 4).

add the intensities of the (unresolved and very close) components on the low frequency side and compare this with the sum for the high frequency side we obtain a theoretical ratio of about 1.22: 1.00. Actually, visual estimation gives a ratio of at least 2:1, if not more (see Fig. 5, λ5610). A similar situation holds for $\pi \cdot Q(4)$ and to a less extent for $\pi \cdot Q(5)$. At present a new densitometer is in process of adjustment and will be used to determine these ratios objectively.[21]

[21] It is possible that the above discrepancy is traceable to the assumption in Kronig's calculations that perturbative terms in H^2 are negligible, whereas this is not necessarily so for very high fields.

4 *Irregular Zeeman effects in higher lines.* In addition to the regular effects produced by the magnetic field in these bands, there are a number of very complex and apparently rather irregular effects confined entirely to lines of large M value. Before it will be possible to attempt any theoretical interpretation of these facts, it will be necessary to make an extended study of the ordinary rotational perturbations present in the Angstrom bands. The magnetic effects in general are confined to isolated lines, or at most to groups of two successive lines in a given branch. They consist essentially of broadening and of splitting of the lines into doublets, in some cases broad and fuzzy and in others very sharp. The size of these patterns is in general of the same order of magnitude as that of the early lines, but in some cases may be nearly twice as great. Usually only two or three such sensitive lines are observed in each band, and these may or may not belong to the same branch. In almost all cases, however, they occur at or near the points in the bands at which large rotational perturbations occur. It seems possible that a systematic correlation of the Zeeman effects and the rotational perturbations may throw light on the origin of the latter, though at the present time the observations show so little regularity that I simply append in Table II a list of the bands and the sensitive lines in each.

TABLE II. *Sensitive lines.*

Band	Sensitive lines
λ5610	$Q(28)$ [Others also- probably]
5198	$P(25)$ $P(26)$ $P(34)$ $P(35)$
4835	$Q(23)$ $(Q24)$
4511	$Q(25)$ [Probably several others]

5 *New bands and analysis of λ4511 band.* In the course of this work a great variety of discharges through CO and CO_2 have been used and on certain of the photographs three or four new bands (always faint) have been discovered. From their simple three-branch nature and their behavior in the magnetic field they can fairly definitely be assigned to the Angstrom system. It is hoped in another paper to give an analysis of these bands together with that of the very important band (0,0) at λ4511. Previous attempts on the latter band have either been unsuccessful[22] or have led to an analysis which Zeeman photographs show in part to be incorrect.[23] This band seems definitely to have more than 3 branches though the extra ones are fragmentary and weak.

In conclusion the author wishes to express his appreciation of the interest in this work taken by Professors R. S. Mulliken and E. C. Kemble and in particular to signify his obligation to the Milton Fund of Harvard University for a generous grant used for experimental expenses.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
December 10, 1928.

[22] E. Hulthén, Thesis, Lund (1923).
[23] Jasse, Compt. Rend. **182,** 692 (1926).

SOME STUDIES IN THE STARK EFFECT FOR THE DIFFUSE LINES OF SILVER AND LITHIUM

By Rufus H. Snyder

Abstract

The Stark effects on the $5^2P_2-6^2D$ and $5^2P_1-6^2D$ groups of silver lines were studied experimentally in some detail by the Lo Surdo method. In the $5^2P_2-6^2D$ group the violet *s*-component was split into two branches, the strong outer one being designated the $^2D_2$ branch and the weak inner one the *F* branch. The red *s*-component had only one branch, that being designated the $^2D_2$ branch. Both the violet and red *p*-components showed only one branch, the $^2D_2$ violet and $^2D_2$ red branch. In the $5^2D_1-6^2D$ group the violet *s*-component was also split into two branches, the strong inner one being designated the *F* branch and the weak outer one the G branch. The single red *s*-component was designated as the $^2D_2$ branch. Both the violet and red *p*-component had only a single branch, the violet *F* and the red $^2D_2$ branch. These results fit better the assignment of Fujioka and Nakamura[1] than did the previous results of Takamine.[2] Microphotometer prints were made from the photographic plates, and the measurements by this method agree closely with direct measurements from the plates. In the lithium spectrum the line λ4602.51A, was resolved into three *s*- and three *p*-components in an electric field, with the violet side having a stronger outer and a weaker inner component for the *p*-vibration; and a weaker outer and a stronger inner component for the *s*-vibration. These results are similar to those of Poirot[3] and Lüssem,[4] obtained by other methods, with the addition of relations between displacements in angstroms and the field strengths. The line λ4132.93 was resolved into three *s*- and three *p*-components, similar to the results of Yoshida.[5]

Introduction

THE Stark effect in the diffuse lines of silver 5^2P-m^2D has been studied by Nagaoka and Sugiura,[6] Takamine,[2] and Fujioka and Nakamura.[1] Fujioka and Nakamura also studied the Stark effect of the diffuse series lines of copper. However some of their results did not seem consistent, so that it seemed of interest to repeat and extend the data already available on these elements. Stark,[7] Howell,[8] Yoshida,[5] Lüssem[4]and Poirot,[3] all have made various observations upon the diffuse series lines of lithium. However only Lüssem[4] and Poirot[3] succeeded in resolving the lines λ4602.51 and λ4132.93 to a greater extent than had been first obtained by Stark. The former used the canal-ray method and the latter used a modified form of canal-ray method in which an additional electric field was applied. So little trustworthy data are available on the Stark effect in the various

[1] Fujioka and Nakamura, Astrophys. J. **65**, 201 (1927).
[2] Takamine, Astrophys. J. **50**, 23 (1919).
[3] Poirot, Le Journal de Phys. **7**, 217 (1926).
[4] Lüssem, Ann. d. Physik **49**, 865 (1916).
[5] Yoshida, Kyoto Mem. College of Science, **3**, 163 (1917–'19).
[6] Nagaoka and Sugiura, Jap. Journ. of Phys. **3**, 45 (1924).
[7] Stark, Ann. d. Physik **43**, 1029 (1913).
[8] Howell, Astrophys. J. **44**, 87 (1916).

elements that it seemed worthwile to find out whether the results on lithium for λ4602.51 and λ4132.93 obtained by Lüssem and Poirot, could be duplicated when the Lo Surdo method is used.

Apparatus and Procedure

The arrangement of apparatus was similar to the one described by Nyquist[9] and Foster[10] in their work on helium and neon, with a few minor changes in the construction of the discharge tube to facilitate the work of dismantling and reassembling the tube.

The spectrograph was assembled in the Physics Department shop. It is the prism type using three glass 60° prisms, four and one-half inches on each side and three inches high, specially made by Gaertner for this apparatus. These are mounted upon a prism table and base made in the department shop. The lenses, which were achromatic, with forty inch focal length, were also supplied by Gaertner. The dispersion for the spectrograph was about 5 or 6 angstroms per mm at H_γ at minimum deviation for sodium light. The exposures for various trials during the research varied from 5 minutes to 5 hours. The width of the spectrometer slit was made as small as the intensities of the spectral lines would permit.

The distance between lines and between the Stark components of the several lines was measured by means of a comparator to the nearest thousandth of a millimeter. Using the Hartman formula $\lambda=\lambda_0+C/(n_0-n)$ the three constants λ_0, c, and n_0 were calculated for each exposure and from this was derived a general expression for the calculation of the wave-length of any line or component of a line. The maximum field-strength for each exposure was determined from the H_β and H_γ lines of hydrogen, which always appear on the plates, due to water vapor in the tube. The field-strengths were determined by comparing the displacements of H_β and H_γ with those given in Stark's original data. Microphotometer records were also made on several lines of special interest. A Moll microphotometer was used.

Results

Silver. In the work on silver, fifteen exposures at various field-strengths were used as the best of a larger number of exposures. Of the silver group only λ4211 was present on some of these plates, while on others, both this group and the group λ4055 were present. On some of the plates the *p*-components are missing, being too weak to measure accurately. On the other hand, several plates gave sharp *p*-components, but the *s*-components are too weak or broad to be measured accurately. The line λ4212.76 was usually broad or faint on the plates examined and its components could not be measured as accurately as the components of λ4210.87, which as a rule were sharper and more distinct.

Several of the best exposures for silver were used to produce microphotometer photographs of the intensity and separation of the components.

[9] Nyquist, Phys. Rev. **10**, 226 (1917).
[10] Foster, Phys. Rev. **20**, 214 (1922).

The results, as obtained from the microphotometer prints, and those actually measured on the plates are in satisfactory agreement. In addition to a check on the accuracy of measurements on the separation of the components, the microphotometer prints give approximate values of the relative intensities of the components. These relative intensities have been indicated by the relative width of the lines in Figs. 1 and 2.

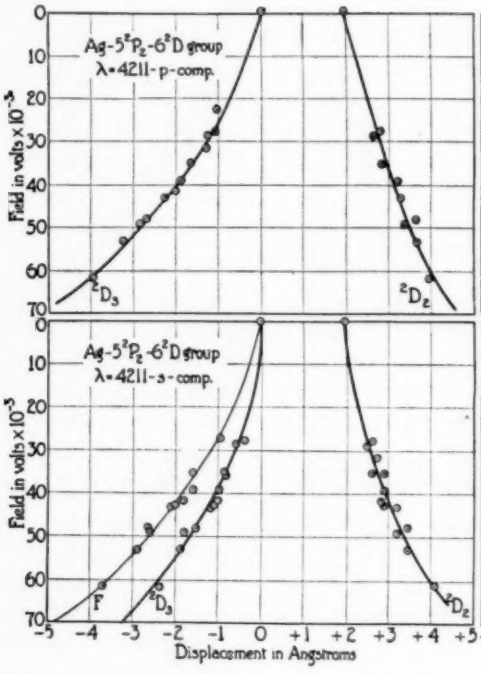

Fig. 1. Relation between electric field and displacement for λ4211 in Ag. Width of curves indicate intensities of components.

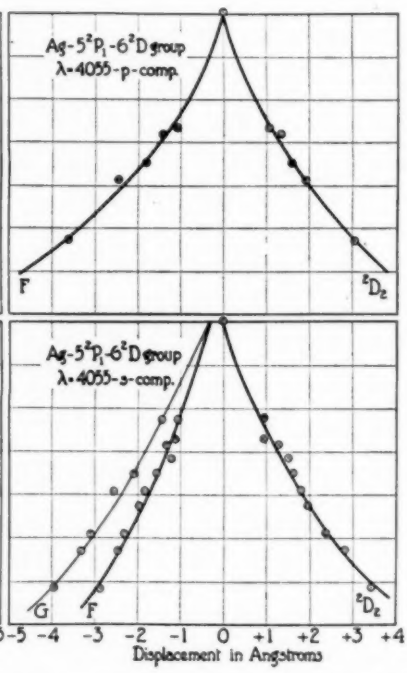

Fig. 2. Relation between electric field and displacement for λ4055 in Ag. Width of curves indicate intensities of components.

The results obtained for silver, shown graphically in Figs. 1 and 2, differ somewhat from those obtained by Takamine. In the first place the displacement is not proportional to the field strength as indicated by Takamine in his diagrams, but the displacement increases more rapidly than field-strengths, a result in agreement with that found by Fujioka and Nakamura for the $5^2P_2-7^2D$ and $5^2P_1-7^2D$ lines. In the next place, there is no indication of a second branch on the red side of the $5^2P_2-6^2D$ group, such as was found by Takamine; a second component is found on the violet side of the group, as seen in Fig. 1. A second component on the violet side of the $5^2P_1-6^2D$ group was also found. This component was marked doubtful in Takamine's paper. Fujioka and Nakamura discuss Takamine's result for the 5^2P-6^2D group and add results for the 5^2P-7^2D and 5^2P-8^2D groups. They point out that in the group $5^2P_2-7^2D$ (λ3810.11) the violet *s*-component of $5^2P_2-7^2D_3$ splits into three branches under the influence

TABLE I. *Results on silver groups. The numbers in parentheses are the relative intensity based on height of microphotometer curves in cm.*

λ=4212.76		λ=4210.87		λ=4055.44 (red)		λ=4055.44 (violet)		E_{max}
$\Delta\lambda-S$	$\Delta\lambda-P$	$\Delta\lambda-S$	$\Delta\lambda-P$	$\Delta\lambda-S$	$\Delta\lambda-P$	$\Delta\lambda-S$	$\Delta\lambda-P$	(volts/cm)
			1.06	0.98		1.02−1.41		22,300
0.74	0.89	0.36−1.04	1.04	0.92	1.07	1.14	0.99	27,100
0.61	0.74	0.56	1.26	1.29	1.40	1.30	1.41	28,500
0.88			1.30	1.54		1.14		31,500
1.06		0.85−1.59	1.63			1.53−2.08 (1.5−1)		35,000
	0.93	0.78	1.61	1.05	1.05		1.75	35,400
1.00	1.33	0.98−1.57	1.85	1.81	1.96	1.81−2.53	1.91	39,000
		1.00−1.76 (1.5−1)	1.91 (3)					41,500
	1.40							42,200
0.97		1.10−1.98		1.96		1.94		42,500
1.35	1.35	1.15−2.12	2.26					43,100
1.55	1.74	1.51−2.63	2.70					48,000
1.31	1.38	1.80−2.60	2.84	2.40		2.28−3.08		49,100
1.55 (2)	1.77 (1.2)	1.89−2.89 (2.5−2)	3.22 (1)	2.86 (1.2)	3.06 (1)	2.43−3.56 (1)	3.56 (1.5)	53,100
2.21 (2)	2.07 (1)	2.36−3.68 (1.5−1)	3.92 (1)	3.45		2.85−3.91		61,500

TABLE II. *Results for lithium group. The number in parentheses are the relative intensity using weakest number of group as* (1).

λ=4602.51				λ=4132.93				
Red *S*	Violet *S*	Red *P*	Violet *P*	Red *S*	Violet *S*	Red *P*	Violet *P*	E_{max} volts/cm
				2.15 (1)	0.07 (3) 2.09 (1)	2.15 (0)	0.27 (3) 3.03 (0)	19,000
0.95	1.99	0.95		2.30 (1)	0.08 (3) 2.38 (1)	2.23 (0)	0.23 (0) 2.66 (0)	20,000
				2.97 (1)	0.27 (3) 3.13 (1)	2.74 (0)	0.27 (3) 3.56 (0)	23,000
1.61				3.06 (1.5)	0.22 (3.5) 2.96 (1)	3.36 (0)	0.44 (3) 3.73 (0)	25,000
				3.16 (1)	0.32 (3) 3.14 (1)	3.35 (0)	0.29 (3) 4.01 (0)	26,000
1.64	1.33		1.33					30,000
2.04				4.10 (1.4)	4.09 (1)	3.76 (0)	0.54 (3) 4.89 (0)	32,000
2.37	2.06 3.08	2.37	3.23					34,000
3.01 (20)	2.68 (10) 3.73 (1)	3.00	2.72 (1) 3.97 (10)					45,000
4.55 (12)	3.47 (10) 5.20 (1)	4.55	4.23 (1) 4.23 (10)					60,000
4.57 (15)	3.94 (10) 5.65 (3)	4.63	4.10 (1) 5.27 (10)					62,000

of the electric field; in the $5^2P_2-8^2D$ group (λ3623.85) the violet s-component of $5^2P_2-8^2D_3$ splits into four branches. If the deductions of Fujioka and Nakamura are correct for $5^2P_2-7^2D$ and $5^2P_2-8^2D$ groups then the violet s-component of the line $5^2P_2-6^2D_3$ of the group $5^2P_2-6^2D$ (λ4211) should contain two branches, and this result is in agreement with the experimental findings. Since other branches of this violet s-component are designated by F, G, H, etc., by Fujioka and Nakamura, then the outer branch of the violet s-component $5^2P_2-6^2D_3$ should be called the F branch, and it is so designated in Fig. 1. In the p-vibration this F branch did not appear but only the single $5^2P_2-6^2D_3$ component, and the other single $5^2P_2-6^2D_2$ component displaced towards the red, as indicated by Takamine.

If we now consider the $5^2P_1-m^2D$ group, we find only the $5^2P_1-7^2D$ group fully discussed in the paper by Fujioka and Nakamura. However, in this group also, the violet s-component $5^2P_1-7^2D_2$ splits into three branches, designated as the $^2D_2$, F and G branches by the authors. The writer found in the $5^2P_1-6^2D$ group (λ4055.44) that the violet s-component splits into two branches. Assuming Takamine's notation as well as that of Fujioka and Nakamura, to be correct, and assuming that $5^2P_1-6^2D_2$ is displaced towards the red side (the writer found a component displaced toward the red side), the two branches of the violet s-component should be designated as F and G branches. They are so designated in Fig. 2. Again the p-vibration has only one branch for the violet component, which will be named the F branch, similar to Takamine's results, the red component being the $5^2P_1-6^2D_2$ branch.

The $5^2P_2-6^2D$ and $5^2P_1-6^2D$ groups, besides other data on silver, show that the F and $^2D_2$ components are quite close together in term value. This indicates that these combinations should about coincide at zero field (see λ4055.44 in Fig. 2). If this is true, $^2D_2$ and F should coincide in group $5^2P_2-6^2D$ (λ4211). Whereas, it appears as if $^2D_3$ and F coincide.

Lithium. The cathode was either a silver or aluminum rod as in previous experiments, with a cup shaped end, into which was pressed the metallic lithium. With this change, the method of procedure was the same as before. It was difficult at all times to sustain a steady field of any great magnitude over the lithium used as the cathode. However, sufficient exposures were obtained to prove that the violet component of 2^2P-4^2D (λ4602.51) is split into two branches, both for the s- and p-vibrations. The line 2^2P-5^2D (λ4132.93) was not obtained often enough, nor under the best conditions for larger field strengths. Thus the resolution was not sufficient to obtain more than the customary three s- and p-components. The results that were obtained for these lines are given in Figs. 3 and 4. In these figures the solid lines indicate the writer's results. Yoshida's values are plotted as broken lines. Howell's one value is indicated by an $\times$ and Stark's one value by a Δ. It will be seen that there is a weak s-component on the outside of the stronger violet s-component just as found by both Lüssem and Poirot, using their respective methods. The writer found only a few indications of the weak violet p-component inside the stronger violet

p-component, which is shown in Fig. 4. The few measurements obtained, as well as those obtained from the microphotometer prints are included in Fig. 3. The intensity relations as given by Lüssem and Poirot do not agree for the line λ4602.51. Poirot found the outer *s*-component of much lower intensity than the intensity found for it by Lüssem. The writer's value compares more favorably with that of Poirot.

For the sake of comparison the values found by Lüssem and Poirot are inserted on the curves. These observations were made by a different method and at higher field strengths than could be obtained by the Lo Surdo method. To make a comparison of the results obtained by Lüssem and Poirot with

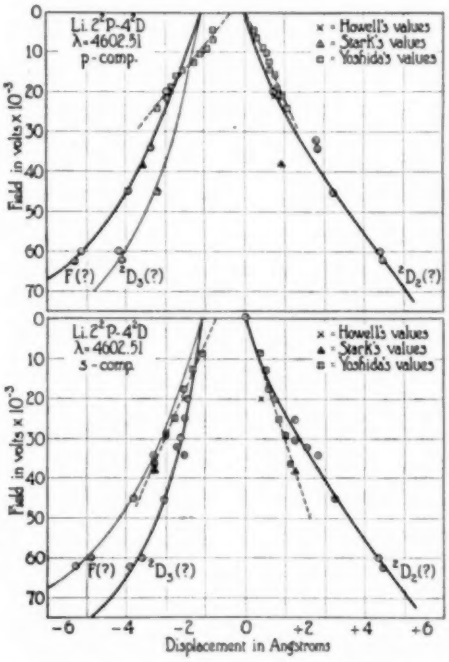

Fig. 3. Relation between electric field and displacement for λ4602 in Li, with a comparison of data. Width of curves indicate intensities of components.

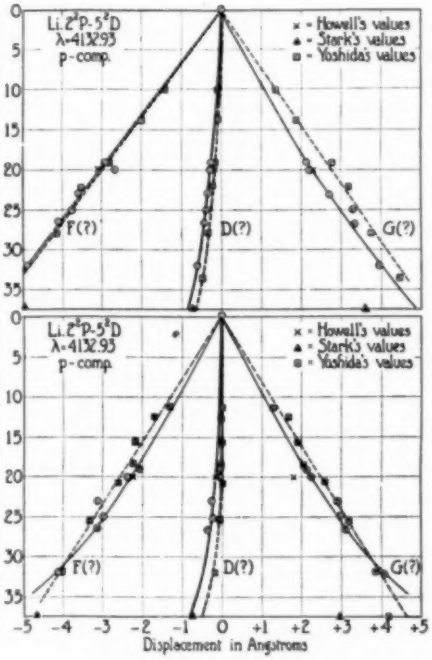

Fig. 4. Relation between electric field and displacements for λ 4132 in Li, with a comparison of data. Width of curves indicate intensities of components.

those obtained in this investigation their results have been plotted in Fig. 5 along with those found by the writer for the line λ4602.51. The displacement in angstroms at a field-strength of 80,000 volts/cm as given by Lüssem are as large as the displacements at 107,700 volts/cm as given by Poirot. From this figure it is seen that Lüssem's values agree very well with those obtained by the writer, while Poirot's values are too small for both *p*- and *s*-components.

The behavior of the 2^2P-4^2D line (λ4602) can be explained by assuming that the effect of the electric field is to make apparent the doublet character of the ^2D terms, which we should expect in spectra of this type. Because the

outer violet component behaves very much like the F component of the silver groups, it has been similarly designated in Fig. 5. Its position at zero field would confirm this statement. The other two components would then be $^2D_2$ and $^2D_3$ and by analogy with the silver group $5^2P_2-6^2D$, the red component would be $^2D_2$ and the inner violet component $^2D_3$. The slope of

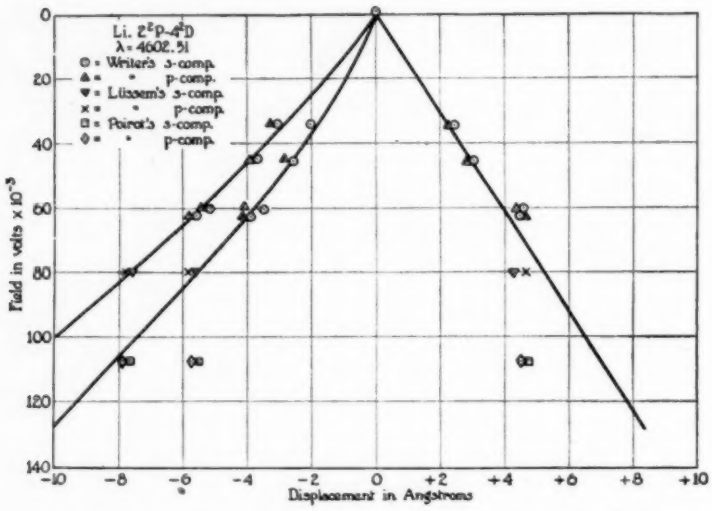

Fig. 5. Comparison of Lüssem's, Poirot's and the writer's data on λ4602 in Li.

the $^2D_3$ component should become steeper towards zero field as is the case with silver.

In conclusion, the writer wishes to express his grateful appreciation to Dr. Alpheus W. Smith, under whose direction this research was carried out and to Dr. J. B. Green for help in the interpretation of the results.

MENDENHALL LABORATORY,
OHIO STATE UNIVERSITY.
August 31, 1928.

THE TEMPERATURE DEPENDENCE OF ELECTRON EMISSION UNDER HIGH FIELDS

By William V. Houston

Abstract

An expression showing the temperature dependence of electron emission under high fields is secured by combining the results of Fowler and Nordheim with the Fermi distribution of velocities used in the Sommerfeld electron theory of metals. The result is similar to that obtained previously by considering the diminution of the work function by the field. The temperature variation is small and decreases as the external field increases. It is of the right order of magnitude to agree with the most recent observations.

IN CONNECTION with the Sommerfeld application of the Fermi statistics to the electron theory of metals it was shown that the very small temperature effect in the emission of electrons under intense electric fields could be expected from the degenerate nature of the electron gas.[1] At that time no attempt was made to study the effect of the field on the emission, and it was assumed merely that the external field decreased the work necessary for an electron to escape from the metal. To estimate the order of magnitude of the effect, Schottky's[2] method was used. Since then, Fowler and Nordheim,[3] and Oppenheimer[4] have made computations, with the wave mechanics, which show the effect of the field in helping electrons to escape. This work shows that electrons may escape even when their energy is less than that required classically to pass through the surface. Fowler and Nordheim recognized that their work, combined with the Fermi velocity distribution, would give a small temperature effect, although they did not determine it explicitly. Oppenheimer started with the picture of a single atom, rather than that of an electron gas, so that a temperature effect was not so directly evident. It is the purpose of this note to give the first approximation to the temperature variation by combining the results of Fowler and Nordheim with the distribution of electron velocities used by Sommerfeld.

Sommerfeld[5] gives the number of electrons per unit volume whose velocity components lie in the element $d\xi d\eta d\zeta$ as

[1] W. V. Houston, Zeits f. Physik **47,** 33 (1928).

[2] W. Schottky, Zeits f. Physik **14,** 63 (1923). A. T. Waterman, Proc. Roy. Soc. **A121,** 28 (1928), considers that an additional diminution of the work function would be produced by the surface charge present under the external field. However, this question is rather difficult to handle because of our inadequate knowledge of the work function itself. He also points out a number of difficulties in the way of this type of interpretation of the field currents. Some of these are met by the treatment of Nordheim and Fowler.

[3] R. H. Fowler and L. Nordheim, Proc. Roy. Soc. **A119,** 173 (1928).

[4] J. R. Oppenheimer, Proc. Nat. Acad. **14,** 363 (1928).

[5] A. Sommerfeld, Zeits f. Physik **47,** 1 (1928) Eq. (19).

$$dn=2\left(\frac{m}{h}\right)^3\frac{d\xi d\eta d\zeta}{(1/A)e^{mv^2/2kT}+1} \tag{1}$$

where $\log A=W_i/kT$ and $W_i=(h^2/2m)(3n/8\pi)^{2/3}$.

Here n is the total number of free electrons per unit volume, while v represents the total velocity of the electrons. To find the total number of electrons with a velocity in the x direction which lies between ξ and $\xi+d\xi$ we may change to cylindrical velocity coordinates ξ, ρ, ϕ. Equation (1) then gives

$$\frac{\partial n}{\partial \xi}d\xi=4\pi\left(\frac{m}{h}\right)^3 d\xi\int_0^\infty\frac{\rho d\rho}{(1/B)e^{m\rho^2/2kT}+1} \tag{2}$$

where $B=Ae^{-m\xi^2/2kT}$. Let $m\rho^2/2kT=v$ and $e^v=w$. Then

$$\frac{\partial n}{\partial \xi}d\xi=\frac{4\pi m^2kT}{h^3}d\xi\int_1^\infty\frac{dw}{w}\frac{B}{w+B}=\frac{4\pi m^2kT}{h^3}\log(1+Ae^{-m\xi^2/2kT})d\xi \tag{3}$$

From Eq. (3) we may write the current emitted by a surface normal to the x axis, due to electrons whose velocities in the x direction are between ξ and $\xi+d\xi$, in the form

$$dI=(4\pi mekT/h^3)\log(1+Ae^{-W/kT})D(W)dW \tag{4}$$

where $W=m\xi^2/2$. $D(W)$ represents the fraction of the electrons of kinetic energy W, incident on the surface, which escape from the metal. Fowler and Nordheim give for this (reference 3, Eq. 18)

$$D(W)=(4/W_a)W^{1/2}(W_a-W)^{1/2}e^{-4\kappa(W_a-W)^{3/2}/3F} \tag{5}$$

In this expression W_a is the potential jump at the surface of the metal in Sommerfeld's notation, F is the applied external field expressed in ergs per cm, and $\kappa^2=8\pi^2m/h^2$. The current coming from the metal is then

$$I=(16\pi mekT/W_ah^3)\int_0^{W_a}\log(1+Ae^{-W/kT})W^{1/2}(W_a-W)^{1/2}e^{-4\kappa(W_a-W)^{3/2}/3F}dW \tag{6}$$

The integral is from $W=0$ to $W=W_a$, since (5) is valid only in this range. The current due to electrons for which $W>W_a$ is the ordinary thermionic current and is negligible for fields at which (5) is valid.

Fowler and Nordheim give the integral of I when $T=0$. To expand in terms of T we may take the derivative with respect to the temperature. Since this derivative is different from zero only in a small region around $W=W_i$, we may remove the terms independent of T from the integral sign and write

$$\frac{\partial I}{\partial T}=\frac{16\pi mek}{W_ah^3}W_i^{1/2}(W_a-W_i)^{1/2}e^{-4\kappa(W_a-W_i)^{3/2}/3F}$$
$$\int_0^\infty\left\{\log(1+Ae^{-W/kT})+\frac{(W-W_i)/kT}{(1/A)e^{W/kT}+1}\right\}dW \tag{7}$$

This can be integrated by the methods given by Sommerfeld[5] and gives

$$\frac{\partial I}{\partial T}=\frac{16\pi^3}{3}\frac{mek^2T}{W_a h^3}W_i^{1/2}(W_a-W_i)^{1/2}e^{-4\alpha(W_a-W_i)^{3/2}/3F}. \tag{8}$$

The second derivative was found to be negligible, at least up to temperatures of 2000°. The expression for the current may then be written as

$$I=\frac{e}{2\pi h}\frac{W_i^{1/2}}{W_a(W_a-W_i)^{1/2}}e^{-4\alpha(W_a-W_i)^{3/2}/3F}\left\{F^2+\frac{32\pi^4mk^2}{3h^2}(W_a-W_i)T^2\right\} \tag{9}$$

This equation shows the same type of temperature variation as the treatment previously given. The temperature variation is small and decreases as the external field increases. As in the previous treatment there is no term containing the first power of the temperature. The coefficients are of the right order of magnitude to agree with the most recent observations.[6] Thus we may repeat the principal conclusion of the former work, that the Sommerfeld electron theory of metals definitely predicts that the emission of electrons under very high fields shall be almost independent of temperature, and that the temperature dependence shall decrease as the field increases.

NORMAN BRIDGE LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
December 4, 1928.

[6] Mr. Lauritsen has kindly told me that his most recent observations in this laboratory definitely show a temperature dependence of the order of magnitude given in Eq. (9). N. A. de Bruyne, Proc. Camb. Phil. Soc. **24**, 518 (1928) interprets his data as showing that the electron emission under high fields is entirely independent of temperature. However, the predicted temperature dependence is of the same order of magnitude as the dispersion of his measurements.

IONIZATION OF GASES BY POSITIVE IONS

By Richard M. Sutton

Abstract

With a tube of simple design, positive ions of potassium are driven by controllable accelerating potentials up to 750 volts into neon and argon at various pressures. Small collecting potentials are adjusted in such a way as to eliminate practically all secondary effects due to the ions, enabling the collection of any electrons liberated by ionization in the gases. Pressure ranges between 0.05 and 1 mm give definite variation of ionization with pressure. Curves are given showing the variation of ionization with pressure and the number of new ions formed per positive ion per cm path reduced to 1 mm pressure. Ionization by this process does not offer a sharp initial point, but a measurable amount is present in neon at 100 volts, and in argon between 100 and 150 volts. The efficiency of the effect is decidedly less than for electron bombardment in these gases; it is several fold greater in argon than in neon. In neither gas has the efficiency reached a maximum at 750 volts, although there is evidence in the case of argon that the maximum efficiency may be found at a slightly higher accelerating potential. The pressure range within which the ionization effect shows itself is higher than should be expected from kinetic theory, which seems to indicate the presence of long mean free paths for the positive ions in accord with results of other observers using magnetic analysis apparatus.

SEVERAL attempts have been made in the past to determine whether positive ions of small energy are effective in ionizing gases. There seems to be considerable disagreement in the results of these attempts and few unambiguous positive results. L. B. Loeb[1] has cited fairly complete references to the subject of positive ion ionization; the reader is referred to his paper for a summary of the previous work in this field. It is well known that canal rays which have passed through potential drops of 10,000 volts or more are capable of producing intense ionization; the theory of this process has been treated by Bohr,[2] J. J. Thomson,[3] and others, particularly for the case of alpha-particles. Ionization in this region seems to be due largely to the action between electric charges in which the relative masses of the impacting bodies plays comparatively small part. In the range below 1000 volts, the evidence is not so clear. The present paper aims to set forth the results of some new experiments on ionization by positives. These experiments show definitely that potassium ions can produce ionization in argon and neon by accelerating potentials as low as 100 volts.

There are three chief secondary effects produced by positive ions which must be accounted for in order to separate ionization from masking phenomena: secondary emission of electrons from metal surfaces in the tube, as treated by A. L. Klein,[4] W. J. Jackson,[5] and others; reflection of positive

[1] L. B. Loeb, Science **66**, 627 (1927).
[2] Bohr, Phil. Mag. **30**, 581 (1915).
[3] J. J. Thomson, "Electricity in Gases," p. 370.
[4] A. L. Klein, Phys. Rev. **26**, 800 (1925).
[5] W. J. Jackson, Phys. Rev. **28**, 524 (1926); **30**, 473 (1927).

ions from the metal parts, studied by G. E. Read,[6] and R. W. Gurney,;[7] and photoelectric effect of excited atoms upon the walls of the tube and the metal parts. Many experimental studies of ionization have been diverted to the study of these effects. W. J. Hooper[8] made attempts to ionize hydrogen with sodium positive ions up to 900 volts and reports negative results. A more recent attempt with hydrogen by Gurney[9] using 7000 volts accelerating potential for K^+ ions, leads to rather inconclusive results. The author's own efforts with hydrogen led to confirmation of Hooper's results. However, in argon, neon, oxygen, and air definite evidence of ionization was found. The efficiency of the process is very low compared to ionization produced by electrons of the same kinetic energy. This difference is due, no doubt, to the relatively large mass of the positive ions and their complex structure which diminishes the probability of transferring sufficient energy upon collision to produce ionization. It is particularly improbable that the energy transferred should go into a single electron, rather than into the change of kinetic energy of the bombarded gas molecule as a whole. In view of the fact that argon gives a much larger effect than neon, it seems likely that the probability of ionization is dependent to some extent upon the number of electrons in the bombarded atom. This point will be tested by the use of other gases.

Apparatus

The tube used in these experiments is shown in Fig. 1. It is an adaptation of a tube constructed in the Norman Bridge Laboratory after a plan drawn up and devised by Dr. Millikan and Mr. Max Wehrli. The source of positive ions was a platinum filament situated in a semicylindrical porcelain trough, coated with a few mg of iron oxide catalyst developed by C. H. Kunsman and described in previous papers. Potassium positive ions from this source were sent by an accelerating potential V_a from the heated anode F, through a 2 mm hole in the cathode C, situated approximately 3 mm above the filament. The cathode was designed completely to enclose the source, thus preventing the escape of positive ions in any but the desired direction. The positives were kept from reaching the collector plate S by means of a small projecting ridge on the cathode which protruded through a circular hole in the collector. One centimeter above the cathode was a wide-meshed grid which was kept constantly at the

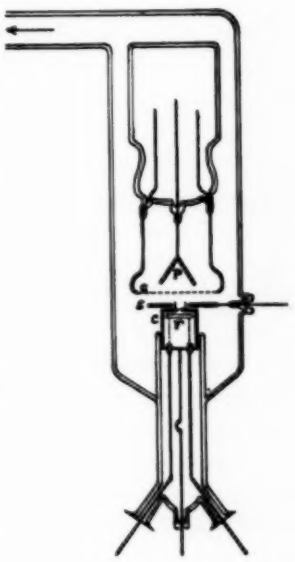

Fig. 1. Positive ion ionization tube.

[6] G. E. Read, Phys. Rev. **31,** 629 (1928).
[7] R. W. Gurney, Phys. Rev. **32,** 467 (1928).
[8] W. J. Hooper, J. Franklin Inst. **201,** 311 (1926).
[9] R. W. Gurney, Phys. Rev. **32,** 795 (1928).

potential of the cathode (ground), so that the space between C and G was field-free except for the bias voltage applied to the collector, never in excess of 13.5 volts. Above the grid was a nickel plate P made in V-shape to prevent reflection of positives. This plate was kept at positive 9 volts to prevent the escape of secondary electrons; this positive potential did not seem to increase the amount of reflection of positives from the plate, as might have been expected to follow. A measureable amount of reflection was found, but this was of small amount and appeared to reach a maximum in the region between 75 and 100 volts, just before ionization set in.

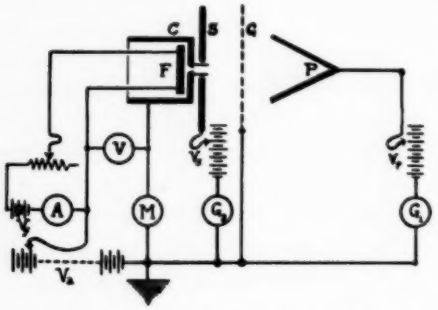

Fig. 2. Wiring diagram for positive ion apparatus.

The electric connections are shown in Fig. 2. A number of different combinations of grid, plate, and collector potentials were tried, but the system shown in the diagram proved most successful since it enables one to reduce the secondary effects to a minimum and collect any products of ionization formed. V_p was generally 9 volts positive to prevent secondary electrons reaching S; V_2 was always kept approximately 4.5 volts higher than V_p, so as to collect any electrons liberated between G and S. The only electrode from which electrons might reach S directly was the grid. The area of metal presented by it to the positive ion stream was exceedingly small. The primary ion current arriving upon the plate, I_p, was recorded by galvanometer G_1 having a sensitivity approximately 10^{-9} amp./mm. The electron current to S, I_2 was measured by a higher sensitivity galvanometer G_2 (10^{-10} amp./mm.) The heating current to the filament, usually about 7 amperes, was supplied by a heavy duty storage battery. It was easy to get pure positive ion emission as high as 10^{-6} amperes, but lower emission was usually used to insure steadiness of the source.

A two-stage mercury diffusion pump backed by a Hyvac served to reduce the pressure to at least 10^{-5} mm whenever desired. Pressures were read on a McLeod gauge connected to the apparatus between the pumps and liquid air trap. Liquid air or solid CO_2 were used at all times to exclude water and mercury vapor. The neon and argon were purified by sputtering for hours at low pressure in a magnesium arc. When clean, they could be admitted to any desired pressure into the experimental tube after the tube was separated from the pumps by a mercury cut-off.

Method of Measurement and Results

Several runs were made to determine what effects of secondary emission and reflection were present. In general the results of these runs confirmed previous observations on the subject. It was found that both effects could

be observed when the potentials of the electrodes were adjusted favorable to them. Fig. 3 indicates the amount of both these effects present at low pressure: Curve 1 showing approximately 7 percent secondary emission at 750 volts accelerating potential with the potential of plate and collector arranged to get a maximum effect; Curve 2 showing less than 1 percent reflection with plate and collector potentials reversed; Curve 3 showing the amount actually present in the experiments when plate and collector potentials were both positive. It will be seen that positive reflection is greater at low values of V_a and secondary emission relatively greater in the higher range, but the total secondary effect at any voltage does not exceed 1 percent of the primary ion emission. The steep increase of Curve 2 near the zero of voltage is natural, as here the accelerating potential of the positives is less than the retarding potential upon the plate which causes the whole ion stream to fall upon the collector S. Both reflection and secondary emission could be increased by cleaning the electrodes, but it was found favorable to let them absorb gas and thus reduce the effect due to them to a minimum. Between runs with different gases, the tube was thoroughly baked out; it was frequently evacuated to very low pressure during the experiments to prevent the accumulation of contaminations emitted by the filament or other sources.

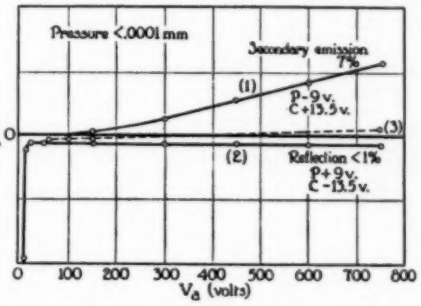

Fig. 3. Reflection and secondary emission at low pressure. Curve 3 shows effect present when $P = +9$, $C = +13.5$ volts.

The accelerating potential, V_a, applied between the anode and cathode, could be varied continuously from zero to 750 volts, the maximum employed in these observations. V_p and V_s were maintained constant during each run and were kept purposely small so as to minimize the possibility of ionization by electron impact. It is important to note that the maximum electron voltage possible within the region where ionization was measured did not exceed 13.5 volts, which is not sufficient to ionize either argon or neon. By maintaining V_s 4.5 volts higher than V_p, reflected ions were kept from reaching the collector unless they were reflected with energy in excess of 4.5 volts. The shape of the plate P also helped to prevent reflection in the direction of S.

Fig. 4 shows curves obtained from neon at various pressures. The curve for the lowest pressure indicates what part of the effect was due to secondary effects other than ionization; for at pressures as low as 0.0001 mm relatively few impacts between positive ions and gas atoms would occur. Any effect present at this pressure must then be due to electrode emission, and it might be reasonable to expect that it is at least as large at this pressure as it would be at higher pressures. As the gas pressure is raised, a distinct increase in the observed current to S is apparent. These curves are obtained by varying V_a, observing at the same time the values of G_1 and G_2 currents. The ratio

of currents to the two galvanometers, I_s/I_p, is plotted against the accelerating potential.

I_p represents the current of initial positive ions from the filament to fall upon the plate, diminished by any reflection of positives or by the arrival of electrons upon the plate due to ionization in the region between G and P, since the potential upon P is such as to collect electrons. Any secondary electrons which succeed in getting away from P would tend to increase the observed value of I_p. I_s represents electron current to the collector plate. Should scattered positives succeed in reaching S against the 13.5 volt retarding field, they would cause a decrease in I_s, or a complete reversal as may be noted over a short range of voltage just before ionization sets in.

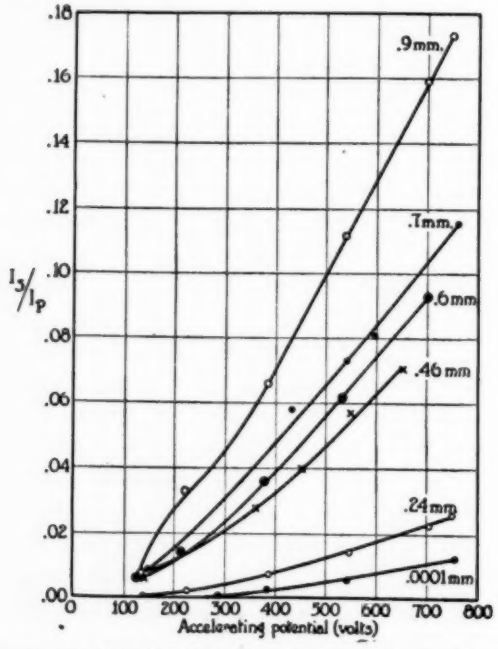

Fig. 4. Curves showing ionization in neon at several pressures. (Ratio of current to collector to current to the plate, plotted against accelerating potential).

Any electron current reaching S must come from the products of ionization between G and S, or from secondary emission from the grid. The latter effect should be a maximum at low pressure, whereas the former will show definite dependence upon the pressure. The ratio of I_s/I_p should therefore be a measure of the ionization produced per positive ion emitted through the hole in the cathode. That this ratio depends directly upon the gas pressure and upon V_a, but is essentially constant for wide variations in I_p, is considered evidence of an ionization effect apart from secondary effects upon the electrodes. An increase of one hundred-fold in the value of I_p causes less than 3 percent increase in this ratio; it was found possible to maintain I_p nearly constant over long periods of time so that error from this

source is negligible. The purity of the gases used should exclude the presence of any appreciable amount of ionization by collisions of the second kind such as observed by G. P. Harnwell[10] in these gases by magnetic analysis of the products of ionization.

Argon was treated in similar fashion to neon giving a series of curves very similar to those in Fig. 4, but showing several times as intense ionization for the same accelerating potentials. This fact will appear evident in the average curves shown in Fig. 5. It was found that ionization in argon and neon set in at approximately 100 volts (perhaps a trifle higher for argon), which is over five times the *kinetic energy* necessary to produce ionization in these gases by electrons. The actual *velocity* of the K^+ ion at 100 volts is, however, equivalent to that of a 0.00135 volt electron. It seems of interest

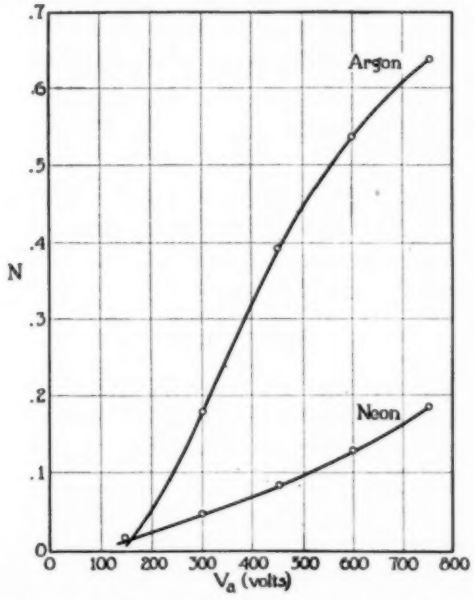

Fig. 5. Plot of N, the number of ions formed per initial positive ion per centimeter path, reduced to 1 mm pressure.

to compare the efficiency of positive ionization with that produced by electrons in the manner used by K. T. Compton and Van Voorhis.[11] Fig. 5, therefore, combines the results of a large number of curves similar to those in Fig. 4 for each gas taken at various pressures, reducing to a path length of 1 cm and a pressure of 1 mm. Comparing these curves with similar curves given by Compton and Van Voorhis, it will be seen that electrons are most effective ionizers in neon at 340 volts and in argon at 140 volts; whereas positive ions at 750 volts have not reached a maximum. The curve for argon indicates that this maximum efficiency might be approaching; it would be of interest to extend the voltage range to see whether the curves for positive

[10] G. P. Harnwell, Phys. Rev. **29**, 583 (1927).

[11] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26**, 436 (1925).

ion bombardment have the same characteristics as those for electrons. Even at 750 volts, the efficiency observed is less than 7 percent of the efficiency recorded by Compton and Van Voorhis, at the maxima for these gases, using electrons as the ionizing agent.

Although commercial oxygen, hydrogen, and air were used in similar fashion to argon and neon, the results are not plotted since no effort was made to purify these gases. Positive results of ionization were found in the case of oxygen and air, whereas any such effect in hydrogen was not observable over the secondary effects of the ions on the electrodes. It appears doubtful that a heavy positive ion can impart sufficient energy to a hydrogen molecule to ionize it without going to considerably higher accelerating potentials. Pressures in hydrogen were used high enough to show ample effect in the other gases, and accelerating potentials up to the arcing voltage were used without evidence of ionization by the positives. It might be of interest to repeat these experiments using lighter positive ions, as kinetic considerations would indicate a greater probability of transfer of energy to the hydrogen in sufficient quantity to produce ionization if the impacting ion were of smaller mass than potassium. However, if the amount of ionization depends upon the number of electrons in the atom bombarded, this argument will not hold and no appreciable increase of ionization would be found from the use of a lighter bombarding ion. This point is one which should be directly settled by experiment.

Discussion

The sensitivity of the method used in these experiments does not permit the location of an exact ionization potential for positive ion bombardment, nor would one expect to find an exact voltage at which the effect sets in. The very nature of the impacts between bodies as complex as a potassium ion and an argon or neon atom would at least blur the point at which ionization sets in. This has been pointed out by J. Franck,[12] Joos and Kulenkampf,[13] and C. Eckart,[14] who have treated the theoretical aspects of this problem. The observed value of 100 volts is slightly higher than Franck postulates for ionization by positive ion impact, given the proper sequence of events favorable to ionization, but it is at least in the same order of magnitude. It is possible that more sensitive methods of measuring the current to the collector *S* would push this value down a few volts by enabling one to observe the less probable impacts resulting in ionization. However, the slope of the curves as (in Fig. 5) they approach the zero axis indicates a fairly sharp origin of the effect. Any ionization which escaped detection must have been less than 0.001 as intense as the primary positive beam.

It will be observed in Fig. 6, in which the ionization is plotted as a function of the logarithm of the gas pressure, that the effect does not appear in any appreciable extent until the pressure reaches 0.05 mm, at which pressure

[12] J. Franck, Zeits. f. Physik **25,** 312 (1924).
[13] Joos and Kulenkampf, Phys. Zeits. **25,** 257 (1924).
[14] C. Eckart, Science **62,** 265, (1925).

the mean free path of a potassium ion according to kinetic theory is of the order of 1 mm. A large effect is still evident above 0.5 mm pressure, with a corresponding reduction of mean free path. At 0.3 mm pressure more than 50 percent of the ions emitted by the filament succeed in getting through to the plate, which according to kinetic theory would mean approximately 400 collisions per ion without neutralization or appreciable loss of momentum in the forward direction since each positive ion must go against a retarding field of 9 volts to reach the plate. It seems therefore probable that these positive ions have considerably longer mean free paths without suffering appreciable scattering or neutralization than would be expected on kinetic theory. Striking as this result may be, it appears to be in accord with the results of Kennard,[15] and Durbin,[16] who examined this point more carefully by magnetic analysis apparatus and were thus able to measure the amount

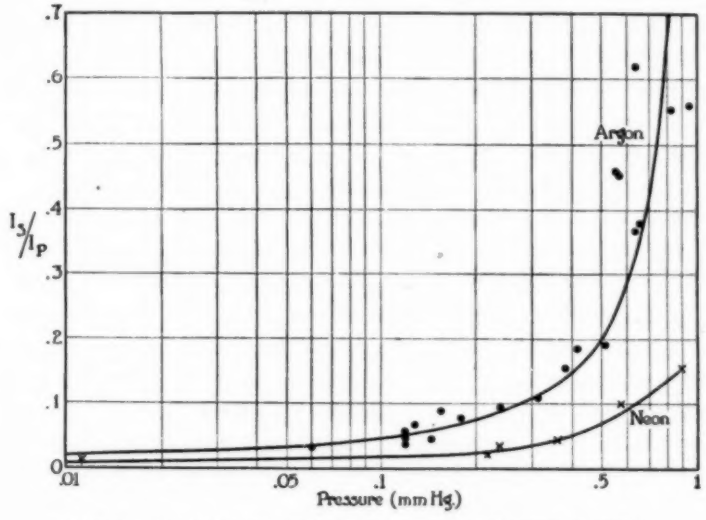

Fig. 6. Variation of ionization in neon and argon plotted against the log of gas pressure.

of loss from the original beam and the loss of energy per ion in traversing the long paths used in their apparatus. It does not agree so well with the results of Harnwell,[17] who used a method which seems less reliable in testing this point than the method of Kennard and Durbin. The writer's results call for the transfer of a larger fraction of the ion's energy upon collision than is allowed in Harnwell's conclusions, as his available 0.002 for neon and 0.005 for argon is not sufficient to cause ionization in either gas within the range of voltages used in this experiment. It seems worth while to investigate this point regarding the mean free path farther and to find, if possible, some adequate explanation for it.

[15] Kennard, Phys. Rev. **31**, 423 (1928).
[16] Durbin, Phys. Rev. **30**, 844 (1927).
[17] Harnwell, Phys. Rev. **31**, 634 (1928).

Neon and argon may be particularly favorable gases to employ since they both have metastable states of long duration; hence there may be some possibility of ionization by multiple impact. The high energy value of these metastable states might cause intense photoelectric effect upon the metal parts in the tube. Any such effect upon the plate would be negligible in aiding electrons to reach S since the potential V_p plus the work function of the metal would exceed the energy available from radiation due to an excited state. Photoelectric effect upon the grid might liberate a few electrons to the collector plate S.

A careful analysis of sources of current to the collecting electrode brings the author to the following conclusions: i) that secondary emission from the metal parts, beyond a possible 2 or 3 percent of the observed effect, is eliminated; ii) that reflection of the positive ions plays a minor part and is evident only within the range from 50 to 100 volts before ionization sets in; iii) that photoelectric effect upon the electrodes (except the grid) plays no effective part by reason of the bias potentials, V_p and V_s used; iv) that ionization by collisions of the second kind plays a negligible part so long as the gases are pure; v) that ionization by electrons liberated from the metal parts cannot take place since there are no potentials in the upper part of the tube high enough to give electrons sufficient energy. Therefore, the currents recorded upon the collector, with the exceptions just noted, are due to electrons liberated within the gas itself by positive ion impact.

It is hoped to extend these experiments to other sources of positives and other gases, and it would seem desirable also to increase the range of potentials up toward the canal-ray region to obtain fuller knowledge of the effectiveness of positive ions as ionizing agents. Any information thus obtained must play a real part in solving the problems of gas discharges.

The writer wishes to express his appreciation of the helpful interest given by Dr. R. A. Millikan during this work, and of the critical suggestions offered by Mr. Willy Uyterhoven.

NORMAN BRIDGE LABORATORY OF PHYSICS,
PASADENA, CALIFORNIA,
December, 15, 1928.

THE PHOTOELECTRIC EFFECT OF MOLTEN TIN* AND TWO OF ITS ALLOTROPIC MODIFICATIONS**

By Alexander Goetz

Abstract

The photoelectric effect of molten tin and two of its allotropic modifications (β and γ) is investigated. An apparatus is described which permits the measurement of the photoelectric emission at the different changes of state. Because of the small photoelectric sensibility of tin, a Hoffmann electrometer had to be used with a sensitivity of ca 10^{-18} coul./sec. The range of temperature was 50°–600°C. The range of wave-lengths from 2300A to 2900A. Taking all precaution to obtain monochromatic light and also taking into account the changes in the absorption of the metal, it was found that the photoelectric emission is independent of temperature as long as the phase of the cathode does not change. On the other hand, a change of state changes very definitely both its intensity and threshold, so that the denser the phase, the larger the work function. The threshold for liquid tin was found at $h\nu_0 = 2925 \pm 10$A; for γ-tin (hexagonal) 2820 ± 10A; for β-tin (tetragonal) 2740 ± 10A. The photoelectric curve of crystallization shows that the hexagonal modification starts to be unstable below $200° \pm 2°$C; and, also, that the speed of transformation is very slow. On account of the fact that the transformation can be followed photoelectrically, it is possible to have a criterion for the cleanliness of the surface. It seems probable that the quantum-equivalent η_e changes also with the phase, so that the denser phase has the larger η_e.

THE photoelectric properties of metals in different phases (liquid and allotropic modifications) have not yet been studied with modern experimental methods so that it has not been possible to decide if there exists a change of the photoelectric constants.

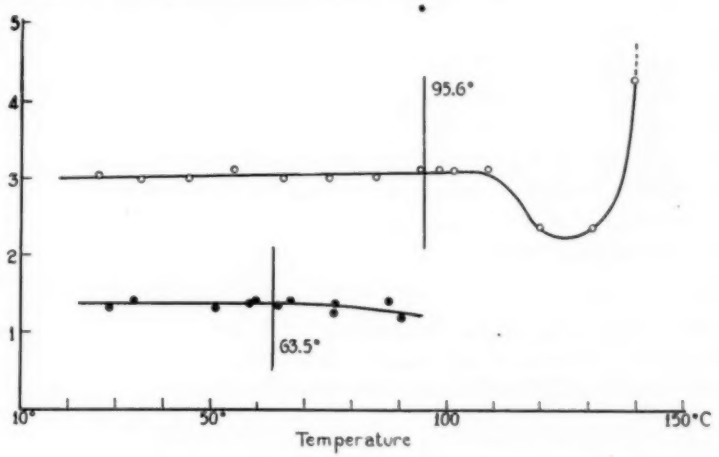

Fig. 1.

* A more detailed description of this subject will be published in the Zeitschrift für Physik.

** Reported at the meeting of the American Physical Society at Pasadena, Calif. December 8, 1928.

The only work which is published about this effect at the melting point is an early paper by Dember[1] dealing with Na and K. The results are shown in Fig. 1. The upper curve shows the values of I_T/I_t as function of T for sodium, the other showing the corresponding values for potassium, where T is the temperature of the cell in which the metal was melted, and t the standard temperature of another cell. There is a large decrease for the Na curve beginning 15° above the melting point, which the author ascribes to the change in the optical surface conditions. But on account of the fact that this author did not use monochromatic light the result cannot be interpreted. Similar investigations have been made by Pohl and Gudden[2] and Roller,[3] both working at the melting point of mercury, but no satisfactory results were obtained.

Recently, Cardwell[4] published a study of the photoelectric and thermionic properties of very carefully outgassed iron, finding a sudden change of the emission at the A_3 point of iron where the body-centered cubic lattice is transformed into the face-centered, but his observation left uncertain whether the change was due to a change in the red limit λ_0 or in the quantum-equivalent η_ϵ.

The theoretical interest of this kind of investigation lies mainly in the question whether the photoelectric effect undergoes, in the transformation from one phase to another, the same alterations observed by Seiliger[5] and the author[6,7,8] for the thermionic emission in this case; since the work of DuBridge[9] and Warner[10] showed the same values for the photoelectric and thermionic work function of platinum and tungsten.

The experiment involved many difficulties, first because the metal had to fulfill unusual conditions which only tin can meet, and second because tin is a very inefficient photoelectric metal. These conditions are:

1. The melting point must be so low that the photoelectric effect can be measured far enough into the liquid phase without being disturbed by the beginning of the thermionic emission.

2. The melting point must be so high that one is not forced to go into regions of temperature where the lifetime of adsorbed gas layers is so long that the probability of obtaining a poisoned surface is too large.

3. The vapor pressure of each phase must be very small.

Tin is probably the only existing metal which fulfills all these conditions well, since its melting point is at 232° and its boiling point lies between 2000° and 2500°. Besides these qualities it has three allotropic modifications,

[1] H. Dember, Ann. d. Physik **23,** 957 (1907).
[2] R. Pohl and B. Gudden not published.
[3] D. E. Roller, Thesis, California Inst. of Technology, 1928.
[4] A. B. Cardwell, Proc. Nat. Acad. **14,** 439 (1928).
[5] S. Seiliger, Dissertation Berlin 1926. Zeits. f. Physik **38,** 443 (1926).
[6] A. Goetz, Phys. Zeits. **24,** 377 (1923); **26,** 206 (1925).
[7] A. Goetz, Zeits. f. Physik **42,** 329 (1927).
[8] A. Goetz, Zeits. f. Physik **43,** 531 (1927).
[9] L. A. DuBridge, Phys. Rev. **29,** 451 (1927); **31,** 236 (1928).
[10] A. H. Warner, Proc. Nat. Acad. **13,** 56, 1927.

of which two are in a safely accessible region of temperature, one being the common white β-tin with a tetragonal lattice,[11] the other the hexagonal brittle γ-form which exists near the melting point. The temperature of the alteration $\gamma \rightarrow \beta$ is not very well known and it is given by the following authors as: Tammann,[12] 203° (at 1000 Atm.); Cohen and Goldschmidt,[13] 170°, 195°; Werigin, 175°, 161°; Smits and de Leeuw,[14] 202.8°; von Simson,[15] 100° (the lowest limit); Smits and Spuyman,[16] 200.3°.

The optical reflectivity of tin is given by several authors. Results are shown in Fig. 2: R_1 being the reflectivity (in percent) measured by Erochin,[17] R_2 by Kent[18] for liquid tin, R_3 by Hulburt[19] for sputtered tin. A_1 and A_2 show the corresponding absorption curves.

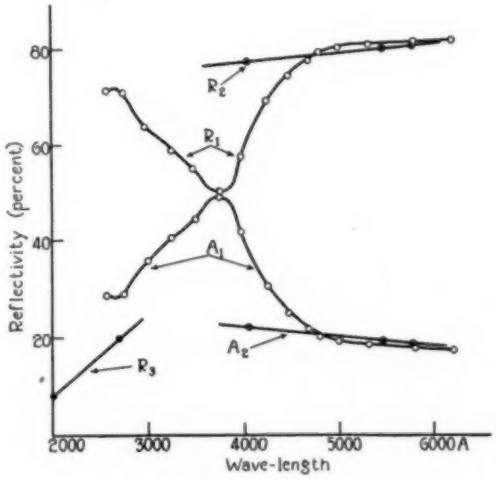

Fig. 2.

The photoelectric threshold of tin at room temperature—which always means the β-modification—is measured by Richardson and Compton[20] as 3620A, by Hennings and Radesch[21] between 2804 and 3132A, by Hamer[22] as 3185A, and recently be Lukirsky and Prilezaev[23] as 3411A. In none of these papers was a method used which really guaranteed a surface free from gas.

[11] M. Polanyi and E. Schmid, Zeits. f. Physik **18**, 75 (1923); Naturwiss. **11**, 256 (1923).
[12] G. Tammann, Drude Ann. **10**, 647 (1903).
[13] E. Cohen and W. Goldschmidt, Zeits f. Physik Chemie **50**, 225 (1905).
[14] A. Smits and H. L. de Leeuw, Verls. Akad. Amsterdam **21**, 661 (1912).
[15] C. von Simson, Zeits f. Physik Chemie **109**, 183 (1924).
[16] A. Smits and J. Spuyman, Verls. Akad. Amsterdam **23**, 687; **29**, 327 (1921).
[17] P. Erochin, Ann. d. Physik **39**, 213 (1912).
[18] C. V. Kent, Phys. Rev. **14**, 459 (1919).
[19] E. O. Hulburt, Astrophys. J. **42**, 205 (1915).
[20] O. W. Richardson and K. J. Compton, Phil. Mag. **24**, 576 (1912).
[21] A. E. Hennings and W. H. Kadesch, Phys. Rev. **8**, 209 (1916).
[22] R. Hamer, Jour. Am. Opt. Soc. **9**, 251 (1924); Phys. Rev. **20**, 198 (1922).
[23] P. Lukirsky and S. Prilezaev, Zeits. f. Physik **49**, 236 (1928).

The arrangement used for this investigation is shown in Fig. 3. The whole apparatus was so constructed that every sealed joint or greased stopcock, etc., was strictly avoided to prevent any chance of vapors of hydrocarbons because of the fact that photoelectric results are only reliable if this condition is fulfilled as perfectly as possible.

The cell *Z*, like the rest of the apparatus, consisted of Pyrex glass. Inside the cell was a cup *V* also made of Pyrex which was supported by the glass stem, through which a tungsten bar *W* was sealed so as to be vacuum tight. *V* contained tin, *W* making a good electric and thermal contact between the cathode and the outside of the tube. The outside end of *W* was welded to the joint of the thermocouple (Pt-Pt-Rh). By this means it was possible

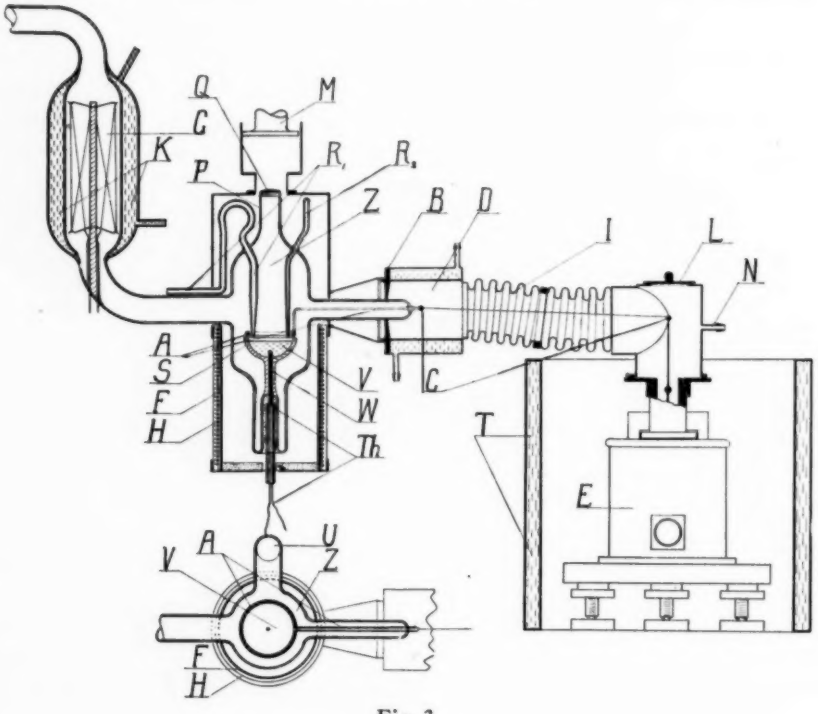

Fig. 3.

to measure the temperature of the cathode at the interior of the metal, which made it possible for one thermally to observe the whole act of crystallization or alteration of the modification. The anode consisted of a thin tungsten wire *A* bent to almost a circle and brought through the side tube to the outside of the cell by means of two Pyrex-tungsten seals. By this construction it was possible to heat the anode by current so that it was easy to outgas the anode at a much higher temperature than the cell would stand. The quartz window *Q* was sealed directly to the cell by means of a transition tube (quartz-Pyrex). The quartz lens on top of *Q* focussed the light from the monochromator *M* at the surface of the tin. The vacuum was obtained by a set of mercury pumps and measured by a dynamic resistance gauge *G*,

whose walls were cooled by means of the cooling jacket *K*. By means of an electromagnetic stop-cock between the liquid air traps and the pumps it was possible to separate the cell from the pumps without danger of adding any new vapors. A trap *U* filled with cocoanut charcoal permitted the absorption of gases when the cell was disconnected from the pumps. The position of the manometer *G* was such that every molecule which came from the cell had to pass through the gauge, causing there a cooling effect regardless of

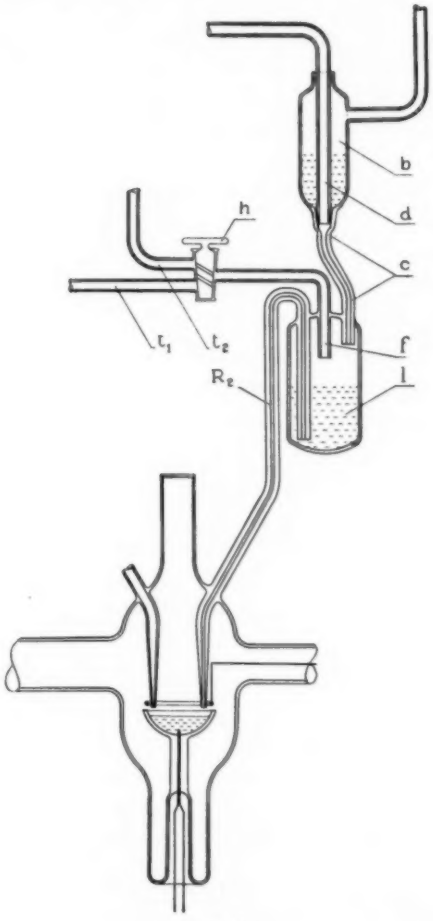

Fig. 4.

the static pressure in the whole apparatus. Thus the progress in outgassing the cathode could be followed rather accurately because it was only necessary to observe the changes which the resistance gauge indicated at the melting point of the metal. The sensitivity of the gauge was obtained by calculation and corresponded to 0.1 ohm per 10^{-7} mm.

Special care had to be observed in filling the cell with tin. The apparatus used for that purpose is shown in Fig. 4. After baking out the cell for 48 hours and reducing the molten tin in the tank *b* by carefully purified hydrogen

at 400°, the tin was filtered through the capillary tube c into the cup of the cell. By this kind of operation the tin went through a very effective reduction and was separated from the light impurities floating on the surface, as well as from the heavy ones sinking down to the bottom of the tank. After the cup was filled the apparatus was sealed off and then the cell was baked out for several weeks before the observations were taken.

The greatest difficulty was caused by the electric measurements, first on account of the high reflectivity of tin in the ultra-violet region, and second by its very small photoelectric sensitivity, which is also expressed by its position in the periodic system between Si and Pb, well known as the metals of the smallest photoelectric activity. Thus none of the usual methods of electrometric measuring was applicable, and it was necessary to use a Hoffmann electrometer,[24] which works in a vacuum and is able to reach the highest sensitivity of any electrical measurement. In this special case the highest obtained sensitivity was calculated as 10^{-18} coul. per sec. ± 50 percent which corresponds to a current between 15 and 20 electrons per sec. To avoid disturbances by free charges of the air it was necessary also to put the lead between cell and electrometer in a vacuum, so the lead had to be vacuum tight; it also had to be a perfect electric shield, flexible so as not to transmit vibrations from the glass apparatus to the electrometer, and a thermal insulator to prevent any conduction of heat from the hot cell to the electrometer. The capacity of this lead had to be less than 2 cm, which is the capacity of the electrometer. The flexibility was obtained by using the flexible seamless copper tubes I, soldered on both ends to the tubes D and L. D had a water-cooled jacket and was sealed with the copper plate B to the outlet tube of the anode. By means of this arrangement it was possible to keep the seal of the anode through the Pyrex at a constant temperature, thus avoiding thermoelectric forces. The part L was sealed to the electrometer E, and was connected by the tube N to the pump. The connection C between cell and electrometer consisted of a copper wire 0.05 mm in diameter. To keep the electrometer at a constant temperature and avoid any influence from the hot cell, E was surrounded by the water tank T.

The rise of the temperature of the cathode was accomplished by heating the entire cell, thus avoiding thermoelectric forces inside the cell and deposits of gas coming from the metal at the glass walls. Therefore the cell was surrounded by a furnace H which was put over a massive metallic tube F. This was in good electric contact with the rest of the electric shields to prevent induced charges by the heating current.

In order to facilitate the cleaning of the surface of the cathode from oxides the tube R_1 was constructed so as to make it possible to send a flow of highly purified hydrogen over the heated surface. This operation, when followed by a very intensive evacuation, should give a guarantee of a clean surface.

[24] G. Hoffmann, Ann. d. Physik 52, 665 (1917).

The electric connections are shown in Fig. 5. K is the cathode, Th the thermocouple, A the anode, N the system of the electrometer above the duants D.

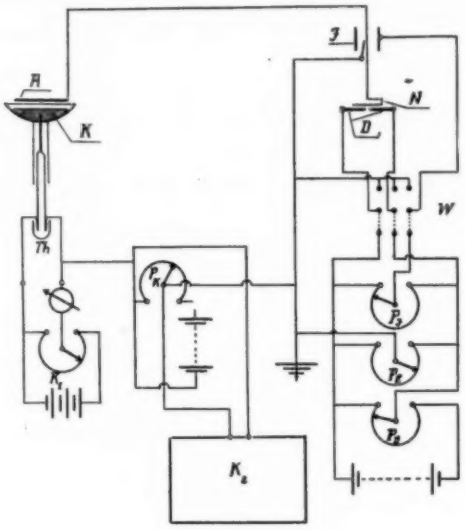

Fig. 5.

The temperature was measured by means of the potentiometer K_1 and a zero-galvanometer, and at the same time one part of Th was used to apply to the cathode a positive potential against the ground, which could be

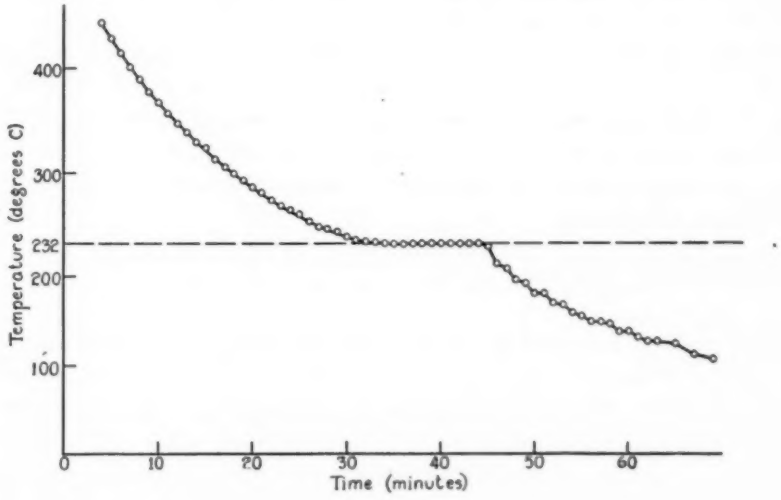

Fig. 6.

measured by the compensation apparatus K_2. The potential of the duants, of the induction ring, J, and the relative position of the ground was adjusted by 3 potentiometers P_D, P_E, P_J, connected by the triple switch W.

The optical arrangement consisted of a mercury arc and a Hilger monochromator M, the first being carefully calibrated.[25]

The cell was filled with liquid tin after a preliminary outgassing of 48 hours, this process being continued over at least 200 hours at 500° after sealing off the filling apparatus. Then the measurements were started.

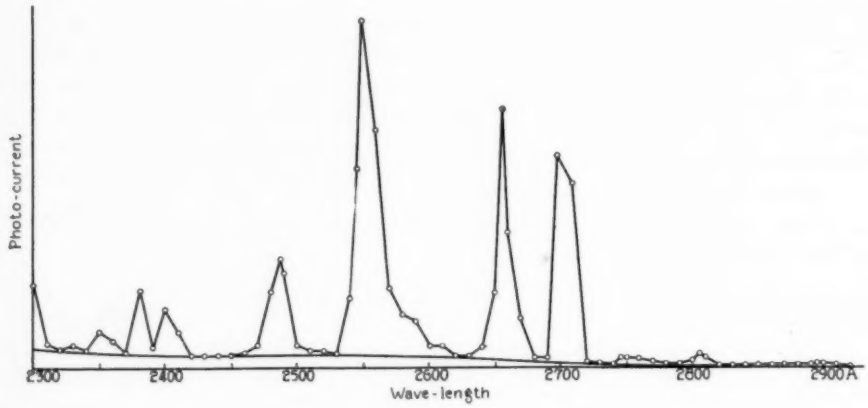

Fig. 7.

To avoid a poisoning of the surface of the cathode by the adsorbed amount of gas, purified hydrogen was let through the tube R_1 (Fig. 3) from time to time, thus reducing the surface at a temperature of 550°.

The cooling curve, Fig. 6, was then measured several times and showed irregulatities below the crystallization which must be ascribed to the mentioned transformation from γ to β tin.

To measure the amount of scattered light the photoelectric emission was measured over the whole spectrum at 5A intervals for liquid tin as shown in Fig. 7. Although the scattered light is immeasurably small (slit aperture of the monochromator 5 mil) in the part of the spectrum which is important for the determination of the thresholds, filters were used in this region but no difference was found.

Two kinds of measurements were taken, first the photoelectric emission at one particular temperature as a function of λ and second the photoelectric emission for one particular line as a function of the temperature. Fig. 8 shows the first curve for three different temperatures where one of the three phases is stable: I for liquid tin at 400°C, II for γ-tin at 210° and III for β-tin at 85°. The absolute values of the emission represented by these curves cannot be compared with each other. The curves with circles give the emission in arbitrary units; the curves with crosses show the corresponding values on the logarithmic scale of the ordinate, as shown in Table I.

These logarithmic curves enable one to extrapolate more exactly the curves in the neighborhood of the red limit, the latter being given by the section of the curve whose tangent is vertical, which allows a more exact

[25] Ch. B. Kazda, Phys. Rev. **26**, 643 (1925).

TABLE I. *Absolute value of the photoelectric emission.*

λ	Liquid tin log I−1	I	γ-tin log I−1	I	β-tin log I−1	I
2301	1.59	3.94	1.38	2.4	1.19	2.04
2378	1.35	2.24	1.18	1.50	1.31	1.30
2399	1.30	2.00	1.09	1.24	1.07	1.19
2482	1.275	1.26	0.943	0.878	0.854	0.715
2537	0.973	0.94	0.774	0.594	0.695	0.495
2653	0.695	0.496	0.480	0.302	0.235	0.172
2699	0.561	0.364	0.305	0.220	0.880−1	0.0758
2752	0.332	0.215	0.0607	0.115	—	—
2810	0.15	0.142	0.544−1	0.035	—	—
2893	0.54−1	0.035	—	—	—	—

plotting of the observations in the region of the disappearing current. The dotted lines in Fig. 7 show the tangents for the logarithmic curves. The red limits thus given for the different phases are shown in Table II.

TABLE II. *Long-wave limit for three modifications of tin.*

No.	Phase	λ_0 (A)	ϕ_0(volt)
I	liquid	2925 ± 10	4.2
II	γ	2820 ± 10	4.38
III	β	2740 ± 10	4.51

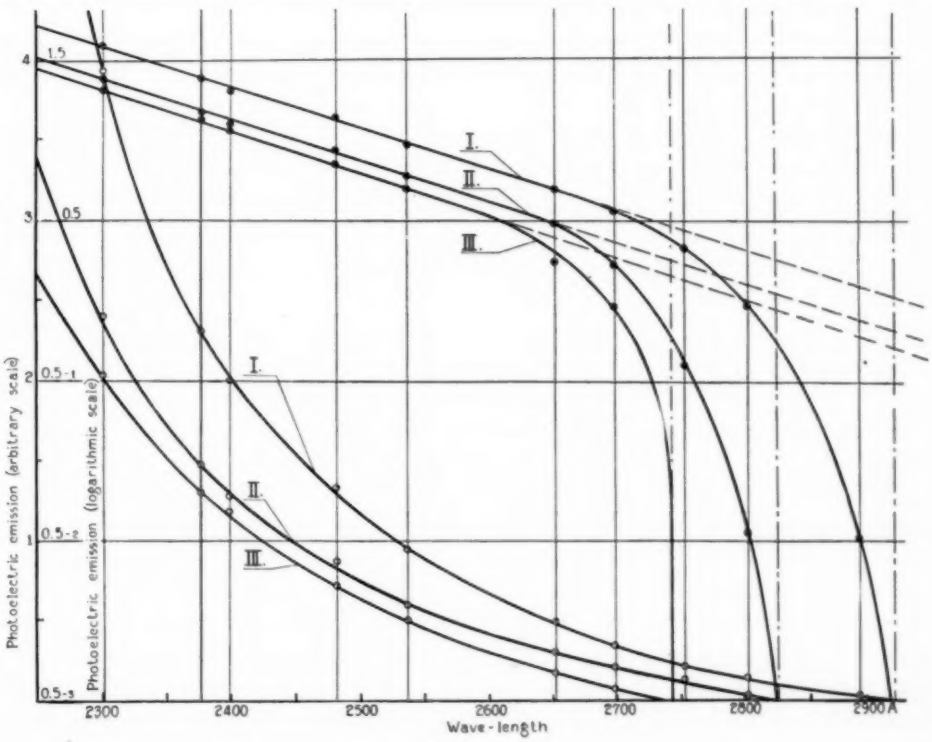

Fig. 8.

The interpretation of the results shown by the photoelectric cooling-curves for different lines is not as easy. From the curves in Fig. 8 one should expect for them three different types, shown in Fig. 9 *a*, *b*, *c*. The case *a* is expected for wave-lengths between λ_0 for liquid and λ_0 for γ-tin, i.e. there should be a region in the spectrum which excites only the liquid tin and none

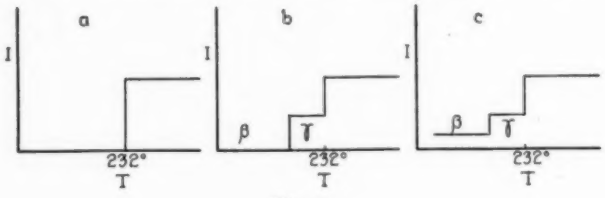

Fig. 9.

of its solid phases. Fig. 9*b* shows the expected effect for λ between λ_0 for γ and β, and 9*c* the cooling-curve for λ smaller then λ_0 for β. No change in the quantum-equivalent η_e at the transformation is considered in these curves.

The measured curves are shown in Fig. 10 (they are selected from ca. 4500 observations with the view to present all possible types of observed

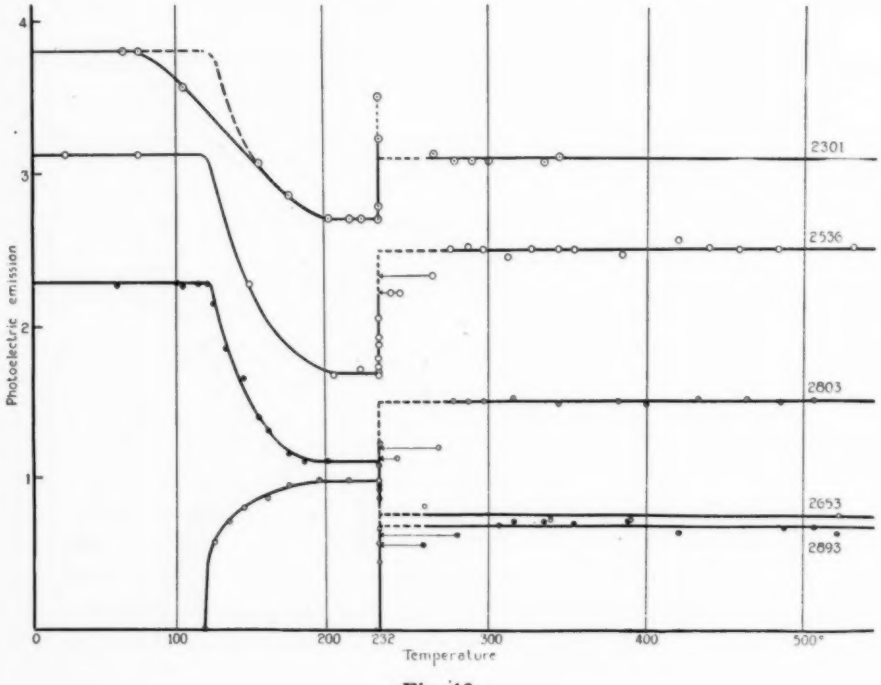

Fig. 10.

curves). The condition *a* is fulfilled for one line (2893A) of the spectrum used, which produced the curve marked with circles in Fig. 10. (The numbers 2893 and 2653 in Fig. 9 have to be interchanged). This curve is in perfect agreement with case *a*.

For the verification of 9*b* there are two lines ($\lambda = 2803$A and 2752A) which show exactly the same effect, wherefore but one is shown in Fig. 10 (2803). This shows the independence of the effect from temperature quite well for the liquid phase over 320°, a drop at the melting point, which is not sudden on account of the thermal lag between the cell and the metal, then a constant emission until 200° and then instead of a sudden disappearance, a slow decline until 120°.

The condition 9*c* should be fulfilled by all the rest of the lines used. The curve $\lambda = 2536$A in Fig. 10 is typical for this region. It looks exactly like the curve of the 9*b*-type for the liquid and the γ phase, but then it rises and reaches a constant value at approximately the same temperature where the other curve became zero. (This curve is one of eight which all showed almost exactly the same effect, therefore it is more certain than the observed points in the curve presented indicate). The curve $\lambda = 2301$A shows qualitatively the same effect but it is very possible that the observation at 102° is wrong.

A type of 9*c* which was observed rather seldom is given for the line $\lambda = 2653$A marked with crossed circles and differs from the ordinary type in that it indicates after a primary decrease of the emission a larger value for the β tin than for the liquid; but the transition from γ to β is the same as in the previous curves.

There are several conclusions one can draw from these results. First, all the curves in Fig. 10 show that *the photoeffect is independent of temperature* over the interval investigated (50°—600°C) *as long as the phase of the cathode is constant.* Furthermore, the case 9*a* being perfectly fulfilled, there is a *change in the threshold between γ and liquid tin. The same is true between the β and γ form* but the observed curves show that *the transformation from γ to β goes slowly* so that a large undercooling effect can be observed. This is in agreement with the fact that the γ tin cannot be detected at all by heating tin up to the melting point; it is shown furthermore by the cooling-curve (Fig. 6) and it gives the explanation for the very different statements of metallographic authors, and could be almost expected from the well-known small speed of the β (white)$\rightarrow\alpha$ (gray) phase-transformation.

The fact that different values of the emission were observed for the solid phase after each crystallization can be explained only by the change of the structure of the surface. The area of the cathode was large compared with the image of the slit of the monochromator at the surface, the latter being ca. 0.5 mm wide. The facets produced by the crystallization had always a different position in relation to the image of the slit which changes the degree of "blackness"; i.e. the absorbed number of quanta is different for each crystallization and therefore the value of the emission of the solid phases relative to the emission of the liquid changes. An example of this fact is the curve 2653 where inspection showed a long groove across the cathode running almost parallel to the image of the slit. In this special case, the cathode acted almost as a black body and the efficiency of the photoeffect was large. In discussing these results one has therefore to distinguish be-

tween two components of η. One, η_0, expresses the "blackness" of the surface and includes also the optical reflectivity shown in Fig. 2; the second describes the electric efficiency of the photoeffect—the quantum-equivalent η_e. The total efficiency is therefore $\eta = \eta_0 \cdot \eta_e$. But there is no way in this kind of measurement (using liquid surfaces) to separate η_0 from η_e directly.

One knows, on the other hand, from the measurement of the optical reflectivity, that there is not very much of a change between liquid and solid tin in the region of the spectrum used. The reflectivity seems to decrease continually with the decrease of λ. No measurement exists for this optical constant as a function of temperature and of a change in the modification. But one should not expect a large change, because the increase in volume at the $\beta \rightarrow \gamma$ transformation is very small. Assuming, therefore, that this change can be neglected, the increase in the photoelectric sensitivity can be explained only by an increase in η_e. The "blackness" of the surface may be changed also to some extent at this transformation, but this effect cannot be large, and especially would not explain that the emission of β-tin is *always* larger than the emission of γ-tin. *It seems therefore very probable that the quantum-equivalent for β-tin is larger than for γ-tin.* It is impossible to make any statement about the transformation from liquid to γ-tin because the change of η is there beyond control.

All these effects could be explained as an effect of gas layers at the cathode, whose conditions of stability are changed by a change in the structure of the cathode; and the history of photoelectric observations shows that even the largest number of precautions and the greatest care are sometimes no guarantee for the reliability of the results. But in this special case there is one effect which shows that a gas layer could *not* explain the results obtained: If the change of the emission were due to a gas layer which forms or disappears at the change of phase, it is inexplainable that the same layer results always in a desensitization at the long wave-lengths and in a sensitization at shorter ones. It would also be hard to explain on that basis that the emission is independent of temperature as long as the phase does not change. Hence it seems impossible that the effect could be caused by gas.

The values of λ_0 obtained for the β phase are much smaller than previous results. (s.a.) This may be an analogy to the decrease of λ_0 with increasing purification as it is observed on platinum.[9] The results can be stated as follows: *The higher the temperature in which one special phase is stable, the smaller is its work function.* Fig. 8 shows that the photoelectric current for wave-lengths ca. 100A smaller than λ_0 after correction for $d\eta_0/d\lambda$ can be expressed in a simple exponential law which is indicated by the linear nature of the logarithmic curves. The cooling-curves indicate that *the point of the transformation of $\gamma \rightarrow \beta$* is at $200° \pm 2°$C which is in very good agreement with other authors.[13,14,16] The speed of transformation is very low at 200° and the photoelectric measurement gives the possibility of measuring the decrease of the γ concentration in the β tin with time and temperature ($\lambda =$ 2803 A); and independently the increase of the β component ($\lambda = 2536$) in the cathode.

Finally it is very probable that the *quantum equivalent increases with the increase of* λ_0 *at the* $\gamma \rightarrow \beta$ *transformation*, and there is no indication that the same does not occur at the melting point. This would give a very interesting analogy between the photoelectric and the thermionic constants, between b and λ_0, A and η_e, because the author[8] found for thermionic effects at the melting point that a change of b always goes together with a change of A, which produces a compensation of the final value of the emission. DuBridge[26] found recently that $ln\ A$ is always a linear function of b for a particular material. Thus it seems to be possible that besides the known and certified identity of b and λ_0 there is an analogy between the thermionic A and the photoelectric quantum-equivalent η_e. But until now we have no other indication than the analogous change of both constants at the change of phase.

In conclusion, the author desires to express his appreciation of the kind interest which Dr. Millikan took in this work and his thanks to Mr. E. McMillan for the valuable help which he gave to the work for one year.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE,
DECEMBER, 1928.

[26] L. A. DuBridge, Proc. Nac. Am. Nat. Academ **14**, 788 (1928).

THE STRAGGLING OF ALPHA-PARTICLES FROM POLONIUM IN PASSING THROUGH GASES

By Henry Eyring

Abstract

The straggling coefficients for alpha-particles from polonium in nine gases have been determined from the ends of the Bragg ionization curves. The value for air of 0.61 mm checks closely that obtained by other methods. The values for polyatomic gases indicate a value greater than the theoretical.

Introduction

In a paper by Gibson and Eyring[1] a method for obtaining the straggling coefficient by using the Bragg ionization curve was outlined. $\pi^{1/2}$ times the subtangent to the ionization curve at the end of the range gives the coefficient α in the equation $y=e^{-(x/\alpha)^2}/\pi^{1/2}\alpha$ directly in millimeters. In this equation y is the fraction of all particles which have a range differing from the mean by x millimeters. This constant α has been designated the straggling coefficient.[2] The term straggling was first introduced by Darwin.[3]

Apparatus and Method

The apparatus used was that described in detail by Gibson and Gardiner.[4] It consists of an upper and lower chamber separated by a sheet of mica approximately 1/100 mm thick. The polonium source rests on the bottom of the lower chamber and the alpha-particles traverse the gas in the lower chamber and the mica between the chambers before emerging into the upper chamber. Here the ions formed were measured by the rate of discharge of a gold leaf electroscope. The rate of fall of the electroscope was plotted against pressure in the lower chamber (the pressure in the upper chamber being kept constant.) The subtangent at the end of the range was then obtained from these curves.

Experimental Results

In the present research the gases in the lower chamber were those whose distribution coefficients were to be determined. Check curves were run and the nature of the checks obtained may be seen in Table I.

The experimental points for a typical C_2H_5Br curve are given in Fig. 1 with the extrapolation to the end of the range and the corresponding tangent and subtangent of the end of the range indicated. The end of the range falls at 0.633 mm. This is the number of millimeters of C_2H_5Br which the average alpha-particle will penetrate under standard conditions of pressure and temperature in addition to the mica. The mica was equivalent to 1.946 cm of air as shown by the fact that the alpha-particles had reached the end of their range after penetrating 1.775 cm of air in addition to the mica.

[1] G. E. Gibson and H. Eyring, Phys. Rev. **30**, 553 (1927).
[2] Briggs, Proc. Roy. Soc. **A114**, 313 (1927).
[3] Darwin, Phil. Mag. **23**, 901 (1912).
[4] G. E. Gibson and and E. W. Gardiner, Phys. Rev. **30**, 543 (1927).

The tangent at the end of the range strikes the pressure axis at 6.53 mm. The length of the subtangent is consequently 0.20 mm. But because of a constant electrical leak (the electroscope discharges at the rate of 0.020 scale divisions per minute) each ordinate in Fig. 1 is too long by 0.020 of a scale division. Correcting the subtangent for this fact we obtain 0.18 for

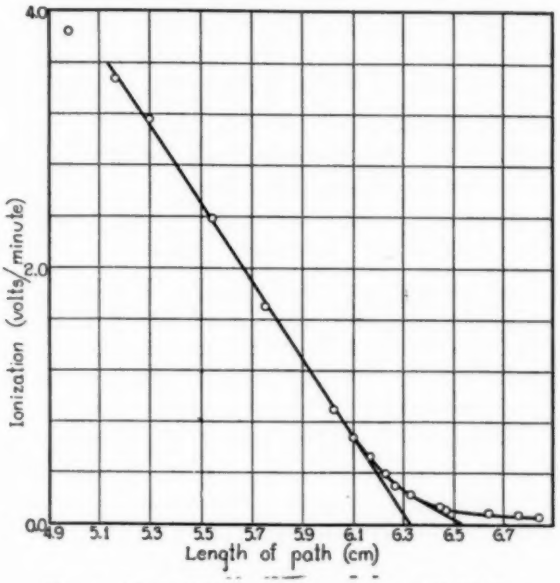

Fig. 1. End of the ionization curve of C_2H_5Br.

its length. Here 0.230 scale divisions per minute is the rate of fall of the electroscope at the end of the range. The value of α, the distribution coefficient, is then $0.18 \times 1.775/0.633 = 0.90$ mm. Multiplication by the factor 1.775/0.633 (the stopping power of C_2H_5Br) simply converts range in C_2H_5Br to range in air. A comparison of the distribution coefficients in this form is virtually a comparison of the distribution in energy of the alpha-particles at the end of the range in the various gases. The experimental values of

TABLE I. *Experimental values of* α.

Gas	α(experimental)	Average	Bohr theory	Experimental stopping powers
C_2H_4	0.67, 0.66	0.67	0.58	1.31
Air	.61, .65, 0.61	.63	.63	1.
N_2O	.77, .83	.80	.63	1.535
CO_2	.80, .84	.82	.63	1.52
CH_3I	.50, .65, .75, 0.75, 0.55	.61	.81	2.61
C_2H_4Br	.89, .90, .79, .94	.88	.71	2.81
C_2H_5I	.68, .93, .91, .76, .90	.84	.77	3.28

α given in Table I are for alpha-particles from polonium at the end of their range which have used up all their energy in penetrating the gas named, except enough to penetrate the mica sheet. The mica sheet as stated has a stopping power equivalent to 1.946 cm of air. α is expressed in mm of air at 0°C and 76 mm pressure.

The column headed Bohr Theory was obtained by taking the experimental value 0.63 for air as the theoretical value also and multiplying this value by the factor[5] $(P_g/P_a)^{1/2}$ to get the value of α for the other gases. In this expression we have $P=4\pi e^2E^2M^2Nn/(M+m)^2$ where e and m are the charge and mass respectively of the electron and E and M the same quantities for the alpha-particle. N is the number of atoms in unit volume of the gas where the pressure is just sufficient to give the gas a stopping power equivalent to air under standards conditions and n is the number of electrons per atom. Thus the expression P_g/P_a is the number of electrons in 1 cc of gas at standard conditions multiplied by its stopping power and divided by the number of electrons in 1 cc of air at standard conditions. The nature of the approximations involved in taking this value for P are treated in detail in Bohr's paper and seem to accord with experimental results at least for the comparison of mica with air as shown by Briggs.[2]

Discussion of Results

An examination of Fig. 8 of Briggs[2] paper shows that the end 1.946 equivalent centimeters of mica will increase α^2 by only about half as much as the 1.775 cm immediately preceding it. But the exact amount seems quite uncertain. In any case if this correction were made, it would alter the results given in the table by only a few percent. For example, the value for air instead of being 0.63 becomes 0.614 mm but this difference is less than the probable experimental error. This corrected value of 0.61 mm checks I. Curie's[6] value of α for polonium of 0.606 mm in air under standard conditions with an exactness which is fortuitious.

A repetition of the experiments for some of the gases would no doubt improve the corresponding values. All values obtained have been recorded since there seemed no adequate experimental reason for discarding any of them. The fact that the values for N_2O and CO_2 are consistent among themselves and with each other points toward a real deviation from the theoretical. Further experiments to test this statement would be desirable. It might be expected that where the atoms are clumped in large aggregates as they are in the case of polyatomic molecules that the distribution would be larger. Methyl iodide seems to be an exception to this rule.

Values of α obtained from some curves by Henderson[7] using the method outlined above give values which seem consistent with those given here for air. The value obtained for Thorium C with a range of 4.538 cm was $\alpha=0.59$ mm.

I wish to thank the Chemistry Department of the University of California, and especially Professor G. E. Gibson, for the use of the ionization chamber.

Chemistry Department,
University of Wisconsin,
December 17, 1928.

[5] N. Bohr, Phil Mag. **30**, 581 (1915).
[6] I. Curie, Ann. de Physique, **10**, 299 (1925).
[7] Henderson, Phil Mag. **42**, 538 (1921).

THE MAGNETIC SUSCEPTIBILITIES OF SEVERAL ORGANIC GASES

By Francis Bitter

Abstract

A method for measuring the magnetic susceptibilities of gases similar in principle to that used by Wills and Hector but simpler in operation was developed. The following results given in molecular susceptibility $\times 10^6$ were obtained: methane (CH_4), -12.2; ethane (C_2H_6), -27.3; propane (C_3H_8), -40.5; butane (C_4H_{10}), -57.4; isobutane (C_4H_{10}), -56.3; ethylene (C_2H_4), -12.0; acetylene (C_2H_2) -12.5; using as standards H_2, -3.94 and N_2, -11.8. These values are in error by less than 4 percent relative to each other. It is shown that the results cannot be reconciled with the assumption that the susceptibility of one of these molecules is equal to the sum of the susceptibilities of the atoms of which it is made up. The hypothesis is suggested that the susceptibilities of these substances are determined by the binding electrons, and it is shown that this assumption leads to a satisfactory interpretation of the observations if the two CH_2 groups of ethylene are supposed held together by electrostatic forces, and the two CH groups of acetylene by a bond similar to the ordinary C-C bond, such as in the C_nH_{2n+2} molecules. It is shown that among the previous measurements of the susceptibility of H_2 and N_2 those made by Wills and Hector are probably the most nearly correct.

DETERMINATIONS of the magnetic susceptibilities of gases were made by a method which is a modification of that developed by Wills and Hector.[1] In principle the latter depended on making a solution of a paramagnetic salt in a diamagnetic liquid such that its volume susceptibility is equal to that of an unknown gas. In operation this method proved rather tedious, and since susceptibilities in terms of other gases were sufficient, it was decided to compare these directly to each other, without making use of an intermediate substance.

Method and Apparatus

It is assumed that the volume susceptibility of a mixture of gases obeys the additive law. More precisely, if the total pressure of a mixture of n gases at the temperature T is P, and the partial pressures of the constituents are p_1, p_2, $p_3 \cdots p_n$, and their respective volume susceptibilities are k_1, k_2, $k_3, \cdots k_n$, then the volume susceptibility K, of the mixture is given by

$$K = (1/P) \sum_{k=1}^{n} p_k k_k. \qquad (1)$$

This equation was tested by Lehrer[2] and found to hold. There seems to be no reason for doubting its validity as long as no chemical reaction takes place within the mixture, and the measurements are made at normal temperatures and pressures.

[1] A. P. Wills and L. G. Hector, Phys. Rev. **23**, 209 (1924).
[2] E. Lehrer, Ann. d. Physik **81**, 229, (1926).

In measuring susceptibilities by the method described below use is made of the mechanical force which an inhomogeneous field exerts on atoms or molecules. In the case of gases this manifests itself in a slight pressure difference maintained between regions in and out of the field, and although such small differences are not capable of direct *measurement*, it was found possible to *detect* even smaller ones, and a balance method based on such detection was developed.

In the diagram in Fig. 1, K is a wooden frame surrounding the pole-pieces M of the magnet, and rigidly connected to it. To this frame is attached the microscope F and the manometer containing the constriction E, so that the horizontal branches can be well centered between the pole-pieces and kept there. In the manometer is a liquid containing colloidal particles whose motion can be observed with the microscope. Above one branch is a mixture of two gases, and above the other a third gas. To determine whether the mixture is more or less diamagnetic than the third gas, the gas-water inter-

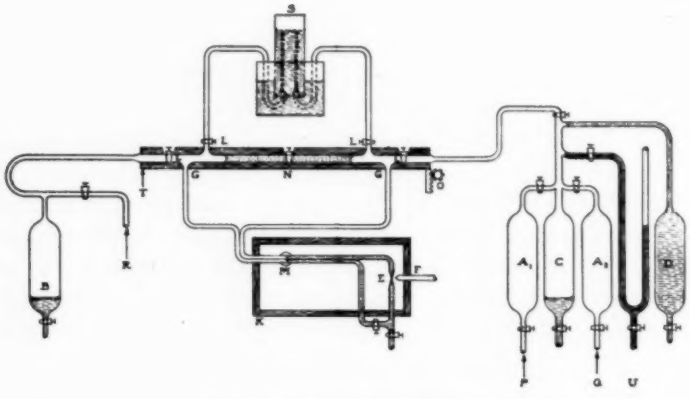

Fig. 1. Diagram of apparatus.

face of both arms is brought between the pole-pieces as indicated in the diagram, and a uniform field H applied. This exerts no force on the liquid of the manometer because of symmetry. But the changes in pressure of the gases when the field is applied will disturb the equilibrium of the system, and from the direction of the deflection of the colloidal particles it can be determined which suffers the greater decrease in pressure, and hence which has the greater susceptibility.

In order to bring the liquid to rest in the above position the following arrangement was adopted. Consider the stop-cocks L closed and the stop-cock N open. Then the arms of the manometer are connected to each other by means of the liquid column surrounding N. The tube containing this liquid is mounted on a board with a hinge at T and a gear at O so that its inclination can be varied, and the liquid column be made to slide to the left or right, thus creating a slight pressure difference between the two arms of the manometer sufficient to bring the liquid to rest. In order to make this part N separately movable, all connections to the stationary parts of the

apparatus were made by means of long fairly flexible glass tubes, about 3 mm in diameter. In order to fill in gases for measurements the liquid in the manometer was raised to the points G, N closed, and L opened, and gases flushed through from the containers B and C into the reservoir S. The dimensions of the apparatus were such that after allowing four or five gallons to flow through the apparatus in the course of about an hour, all traces of air were removed. The gases were then sucked down to M by lowering the liquid in the manometer, the system brought to rest by closing L, opening N, and levelling with O, and an observation made. Two methods to check the assumption of a uniform field over M were employed. Air was admitted to both sides of the manometer, and it was found that over a considerable region within M the manometer suffered no deflections upon application of the field. Suppose that nevertheless the fields over the two arms were not equal $H_1=H+\delta H$, $H_2=H$. Then we have approximately:

$$\delta p_{air}=\delta p_1-\delta p_2=\tfrac{1}{2}K_{air}\cdot 2H\delta H$$

If Δp is the smallest pressure change which can produce an observable deflection, and the largest inhomogeneity present, δH, is such that it will produce, using air, a change in pressure δp_{air}, we have:

$$\Delta p>\delta p_{air}=K_{air}H\delta H.$$

But since the volume susceptibilities of all the gases used were much smaller than the volume susceptibility of air, the change in pressure, δp_x, due to an inhomogeneity δH would be correspondingly smaller, and we have:

$$\Delta p>\delta p_{air}>\delta p_x=K_xH\delta H$$

and the inhomogeneities in the field are not sufficient to affect the results.

In Fig. I, A_1 A_2 and B represent the storage tanks for the three pure gases P, Q, and R. The gases P and Q were admitted to the chamber C in amounts determined by readings on the mercury manometer U. This mixture was then thoroughly stirred by passing it back and forth between the chambers C and D.

Attempts were first made to handle and measure the gases at pressures of about 20 atmospheres, but this proved to involve practical difficulties, mainly in connection with developing suitable valves to replace the stopcocks, and it was found that sufficient sensitivity could be obtained by other means, thus making it possible to keep the apparatus simple and easy to construct and handle.

In order to get conveniently strong fields without resorting to excessive currents, pole-pieces with a small diameter were selected. This was 1 cm and their distance apart 3 or 4 mm. Fields of over 20,000 gauss proved unnecessary, and a current of 15 or 20 amperes through the coils of the large Weiss electromagnet used was ample. The constriction E was chosen very small. Some having inside diameters of 0.05 mm were tried and proved quite feasible. Because of the difficulty of bringing the small particles to rest in

these very small ones, constrictions having inside diameters of about 0.1 mm were actually used. These were drawn so that the constricted portion was as short as possible, thus offering a minimum of resistance to the flow of the liquid in them. Also the walls were made thin so that small particles could readily be seen through them. The particles were obtained by grinding gum mastic into a powder which was stirred into the liquid of the manometer.

The microscope used had a magnification of 150×. The diameter of the manometer tube between the pole-pieces was in the neighborhood of 3 mm. The smallest observable displacement of the meniscus between the pole-pieces can now be calculated. If we assume[3] 1 mm to be the smallest observable displacement in the eye-piece of the microscope, this represents 1/150 mm actual displacement in the constriction, and this in turn is produced by a displacement x of the meniscus given by:

$$x=(0.1)^2/(150\times 3^2)=7.4\times 10^{-6}\text{mm}.$$

In order to produce these deflections with the small pressures available it was necessary to use liquids with a small viscosity, and further, in order to avoid the trouble of having continually to clean the tubes of the manometer, a liquid which wet the surface readily in spite of slight impurities on the walls was desirable. Several were tried, and methyl alcohol finally used. The smallest pressure differences that were observed with this apparatus were of the order of 10^{-3} dynes/cm^2.

Measurements and Materials

Hydrogen and nitrogen were used as standards. Since the susceptibility of all gases measured was greater than that of nitrogen, the procedure was to dilute the unknown gas with hydrogen and to determine for what concentration the volume susceptibility of the mixture was equal to that of nitrogen. In determining the following results the values used for the susceptibility of hydrogen and nitrogen are those given by Wills and Hector[4] which are:

$$\chi(N_2)=-11.8\times 10^{-6}\ ;\quad \chi(H_2)=-3.94\times 10^{-6} \tag{2}$$

All the gaseous members of the methane series were measured, as well as one gas, ethylene, with a double bond, and one gas, acetylene, with a triple bond. The values are given in Table I.

Table I. *Molecular susceptibilities of various gases.*

Gas		$\chi\times 10^6$	Gas		$\chi\times 10^6$
Methane	CH_4	−12.2	Isobutane	C_4H_{10}	−56.3
Ethane	C_2H_6	−27.3	Ethylene	C_2H_4	−12.0
Propane	C_3H_8	−40.5	Acetylene	C_2H_2	−12.5
Butane	C_4H_{10}	−57.4			

[3] 1 mm is about the smallest apparent deflection that could be observed because the particles were never actually at rest.

[4] L. G. Hector, Phys. Rev. **24**, 418 (1924), and reference 1.

In Fig. 2 are plotted along (*A*) the above results for the methane series. The points for hexane, octane, and decane, indicated by solid triangles, were measured by Pascal[5] on substances in the liquid state. Pascal used water as his standard, and assumed -7.5×10^{-7} to be the proper value for its specific susceptibility. The value at present accepted is -7.2×10^{-7}, and this was used in the work of Wills and Hector[1] in their determinations of hydrogen and nitrogen. The values plotted are therefore Pascal's observations reduced in the ratio 7.2/7.5. The points for pentane, hexane, and heptane, indicated by solid circles, are observations by Vaidyanathan[6] on substances in the vapor state.

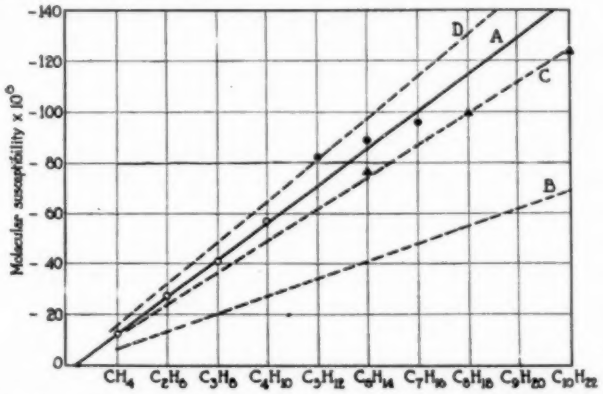

Fig. 2.. Molecular susceptibility as a function of molecular composition. The solid circles are measurements by Vaidyanathan on substances in the vapor state. The solid triangles are measurements by Pascal on substances in the liquid state. The points for methane, ethane, propane, and butane represent measurements in terms of H_2 and N_2 described in this paper. The points as plotted along line *A* are based on susceptibilities of H_2 and N_2 as measured by Wills and Hector. Using values for H_2 and N_2 found by other observers these measurements would lie along lines *B*, *C*, and *D*.

Of the gases measured, the methane series was furnished by the Carbide and Carbon Chemical Corporation. The impurities in the propane, butane and isobutane were guaranteed to amount to less than 3 percent. The methane and ethane, however, had no guarantee, and it was stated that they contained considerable portions of each other as impurities. An analysis was therefore undertaken, and carried out in the laboratories of Dr. Lincoln T. Work of the Chemical Engineering Department of Columbia University. The results are given below, the percentage referring to volume.

Methane Sample				*Ethane Sample*			
CO_2	0.0%	CO	0.0%	CO_2	0.2%	CO	0.1%
C_2H_4	0.1%	CH_4	80.7%	C_2H_4	2.3%	C_2H_6	90.6%
C_3H_6	0.3%	C_2H_6	16.1%	C_3H_6	0.5%	H_2	5.7%
O_2	0.2%	N_2	2.6%	O_2	0.3%	N_2	0.3%

The first five gases in each case were tested for by absorption, and the amount of the last three present as impurities determined by explosion with a known amount of oxygen.

[5] P. Pascal Ann. de Chim. et de Phys. [8] **25,** 289 (1912)

[6] V. I. Vaidyanathan, Phys. Rev. **30,** 512 (1927).

The acetylene used was commercial Prest-o-lite acetylene, and to it was attributed by its maker a purity in the neighborhood of 99 percent. The ethylene was furnished by the Ohio Chemical and Manufacturing Co. and was guaranteed to contain less than 0.5 percent of impurities. The standards, hydrogen and nitrogen, were also furnished by the Ohio Chemical and Manufactoring Co., and were of guaranteed purity 99.9 percent and 99.2 percent respectively.

All gases before being admitted to the apparatus were rid of oxygen either by being bubbled through long containers of pyrogallol or by being passed over red hot copper filings, or both. Further, since it was found necessary to use liquids with considerable vapor pressures in the apparatus, all gases were first saturated with the vapors of any liquid with which they came into contact by being bubbled through long tubes containing glass chips and the liquid in question.

The following mixtures were found to have the same volume susceptibility as nitrogen, the percentage referring to volume. "Methane" and "Ethane" refer to the mixtures described above.

71.2% "Methane"	+28.8% Hydrogen	15.0% Isobutane	+ 85.0% Hydrogen
36.0% "Ethane"	+64.0% Hydrogen	98.0% Ethylene	+ 2.0% Hydrogen
21.5% Propane	+78.5% Hydrogen	91.6% Acetylene	+ 8.4% Hydrogen
14.7% Butane	+85.3% Hydrogen		

The results for the last five gases were calculated from these data. The first two had first to be corrected for the impurities by the aid of equation (1). In doing this, the following values of χ were used: for CO_2[7], -18.7×10^{-6}; for C_6H_6[8], -83×10^{-6}.

As a check on the assumption of a uniform field a mixture of propane and hydrogen was balanced against ethylene. This gave:

21.7 percent Propane+78.3 percent Hydrogen

With the value found above for ethylene, this leads to a value for propane of -40.9×10^{-6}, in good agreement with that previously found.

The experimental error in the observations themselves is in every case less than 1 percent. That is, values determined from successive observations never differed by more than 1 percent. The error in the results produced by the impurities may be calculated as follows:

The presence of m percent of an impurity having the susceptibility nK where K is the susceptibility of the gas under consideration will change its susceptibility to K', where

$$K'=\frac{100-m}{100}K+\frac{m}{100}nK=1-\frac{m(1-n)}{100}K.$$

Therefore $m(1-n)$ is the percentage change in the susceptibility produced by the impurity. Since the impurities in the case of the saturated hydrocarbons are almost entirely adjacent members of the series for which n has a value less than 2, and m is less than 3, and since for ethylene and acetylene $0<m<1$, we may say with confidence that in every case the error

in the susceptibility produced by the impurities is less than 3 percent. Thus the total relative error in the results is less than 4 percent.

Discussion of Results

The choice of the values (2) for the susceptibilties of hydrogen and nitrogen can be rendered plausible by the following consideration. Other values are to be found in the literature as follows:

	Molecular Susceptibility $\times 10^6$	
	H_2	N_2
Také Soné[7]	−3.94	−7.4
Wills and Hector[1]	−3.94	−11.8
Glaser[8]	−(3.94)	− 7.4
Lehrer[2]	− 5.0	—
Vaidyanathan[9]	—	−12.9

Glaser measured nitrogen in terms of hydrogen, and the value −7.4 for nitrogen is found by assuming −3.94 for hydrogen. Using Glaser's or Také Soné's values in computing my results for the methane series, it is found that they lie along the dotted line *B* in Fig. 2. This cannot be reconciled with the observations of Pascal and Vaidyanathan for the higher members of the series. Similarly using Lehrer's value −5.0 for hydrogen and the value −11.8 for nitrogen, the line *C* is obtained. And using Vaidyanathan's value −12.9 for nitrogen and −3.94 for hydrogen, the line *D* is obtained.

If it is assumed that the linear relation found for the first four members of this series extends to the higher members in the vapor state, then *A* is surely the best of the four lines in Fig. 2. This is taken as an indication that the values for nitrogen and hydrogen found by Wills and Hector are most nearly correct, and these are consequently used in the calculations.

The results plotted along *A* in Fig. 2 may be represented by the formula:

$$\chi(C_nH_{2n+2}) = (-14.5n+2.0)\times 10^{-6}.$$

(In the further discussion the factor 10^{-6} will be omitted for simplicity). This expresses the fact that in chains of this sort the electronic distribution repeats itself periodically, and that at the ends of the chains certain irregularities manifest themselves and are taken into consideration through the term independent of n. Pascal assumed that the magnetic properties were determined by the atoms themselves and found from many measurements on relatively complex molecules containing carbon, hydrogen, and other atoms that the susceptibility of a compound could be written as the sum of the susceptibilities of the atoms of which it is made up. Carbon and hydrogen were found to have values such that

$$\chi(C_nH_{2n+2}) = -6.0n-2.9(2n+2)$$
$$= -11.8n-5.8.$$

[7] Také Soné, Phil. Mag. **39**, 305 (1920).
[8] A. Glaser, Ann. d. Physik **75**, 459 (1924).
[9] V. I. Vaidyanathan, Phil. Mag. **5**, 380 (1928).

This cannot be reconciled with the fact that for this series the constant term is shown to be positive. An obvious extension is to assume the susceptibility to be a function of the bonds as well as of the atoms. Thus, if χ(C-C) represents the quantity to be attributed to a C-C bond, this would give

$$\begin{aligned}\chi(C_nH_{2n+2}) &= n\chi(C)+(n-1)\chi(C\text{-}C)+(2n+2)(\chi(H)+\chi(C\text{-}H)).\\ &= n[\chi(C)+\chi(C\text{-}C)+2(\chi(H)+\chi(C\text{-}H))]\\ &\quad +2[\chi(H+\chi(C\text{-}H)]-\chi(C\text{-}C).\end{aligned}$$

This is then a possible explanation of the positive constant without having recourse to paramagnetism. A real test of such an assumption cannot be undertaken with the data at present available, and any conclusive interpretation of the results described in this paper must be deferred to some future date when more information is available concerning the susceptibilities of molecules containing relatively few atoms.

Before closing the discussion, however, it is worth inquiring what the application of the above hypothesis to ethylene and acetylene would give. It is assumed that χ(H), χ(C-H), and χ(C) are unchanged, and the above results show that

$$\chi(CH_4)=\chi(C_2H_4)=\chi(C_2H_2)$$

or, after canceling the factor χ(C) from both sides

$$\begin{aligned}4(\chi(H)+\chi(C\text{-}H)) &= 4[\chi(H)+\chi(C\text{-}H)]+[\chi(C)+\chi(C=C)]\\ &= 2[\chi(H)+\chi(C\text{-}H)]+[\chi(C)+\chi(C\equiv C)]\end{aligned}$$

Assuming that paramagnetism does not enter, an assumption which can be regarded only as plausible, and to be judged by its consequences, this would give

$$\begin{aligned}\chi(C)=\chi(C=C)&=0\\ \chi(C\equiv C)&=2[\chi(H)+\chi(C\text{-}H)].\end{aligned}$$

Through elimination in the above equations the following values are obtained:

$$\begin{aligned}\chi(C\text{-}C)&=-8.25\\ 2[\chi(H)+\chi(C\text{-}H]&=-6.25\\ \chi(C\equiv C)&=-6.25.\end{aligned}$$

Evidently, a value different from zero for a bond means that in some way electron orbits are to be associated with it, and a zero value means that this is not the case. Bearing this in mind it is interesting to see that the electrons can be arranged in groups of two in a very simple way, as postulated by G. N. Lewis[10] Heitler and London,[11] and others, for occupied

[10] G. N. Lewis, Valency and Atomic Structure.

[11] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

valences. In the carbon atom the two K electrons form in each case such a group, thus leaving four more to be considered.

With every C-H bond are associated the one electron from hydrogen and one of the L electrons of carbon. This leaves for the end carbon atoms of the saturated chains one electron each, and for the rest two each, and these are exactly sufficient for an arrangement of two for every C-C bond. In the case of ethylene two of the L electrons of each carbon atom are associated with their respective C-H bonds, leaving two to be accounted for in each atom. But $\chi(C=C)=O$ indicates that these do not take part in the bond, and they may thus be considered as forming a closed group of two in their respective L_1 shells, as Heitler[12] assumed for the L_1 electrons of nitrogen in the N_2 molecule. In order that such a configuration should form a molecule it is necessary that the Coulomb forces themselves should give a potential energy curve with a minimum. Until more is known about the structure of the CH_2 group it is impossible to verify this. But that such is possible may be seen from a calculation[13] of the Coulomb forces for the H_2 molecule which show this feature. In acetylene, the value of $\chi(C\equiv C)=-6.25$ of the same order as $\chi(C\text{-}C)=-8.25$ might be taken to indicate that the triple bond is similar to a single bond. This would leave the two L_1 electrons in a closed group of their own, one L_2 electron of each carbon atom associated with the corresponding hydrogen electron, and the remaining two associated with each other in the $C\equiv C$ bond. Exact agreement of the $\chi(C\text{-}C)$ and $\chi(C\equiv C)$ susceptibilities cannot be expected because of the disturbing effect of the L_2 electrons in the latter case, both on the C-C as well as the C-H bonds.

In conclusion I wish to express my indebtedness to Professor A. P. Wills for suggesting the method used in this research.

PHYSICS LABORATORIES,
COLUMBIA UNIVERSITY.
September 1, 1928.

[12] W. Heitler, Zeits. f. Physik **47**, 839 (1928).
[13] W. Heitler and F. London, Zeits. f. Physik **44**, 462, (1927).

THE EFFECT OF TENSION AND A LONGITUDINAL MAGNETIC FIELD ON THE THERMOELECTROMOTIVE FORCES IN PERMALLOY

By Alpheus W. Smith and Joy Dillinger

Abstract

Measurements have been made on the combined effect of tension and a longitudinal magnetic field on the thermoelectromotive force in three specimens of permalloy. The specimens were in the form of wires, the composition being 78, 81 and 84 percent nickel with the remaining part iron. In all cases the magnetic field produces a decrease in the thermoelectromotive force. Annealing at 1000°C increases the change of thermoelectromotive force produced by a longitudinal magnetic field. In an alloy containing 78 percent nickel tension decreases the maximal value of the change of thermoelectromotive force. In an alloy containing 81 percent nickel the maximal value of $\Delta E/E$ is relatively insentitive to tension. In an alloy containing 84 percent nickel tension decreases the change of thermoelectromotive force at low magnetic fields but increases it for magnetic fields greater than about 10 gauss. In all three cases the maximal value of $\Delta E/E$ is relatively insenitive to changes in tension beyond about 10 kg/mm². There is a parallelism between the change of length and change of thermoelectromotive force under the combined action of tension and a longitudinal magnetic field. In high-nickel permalloys tension decreases the intensity of magnetization for low magnetic fields but increases the magnetostrictive contraction and the change of thermoelectromotive force. In low-nickel permalloys tension increases the intensity of magnetization for low magnetic fields but decreases the magnetostrictive expansion and the change of thermoelectromotive force.

Introduction

A STUDY of the effect of tension on the intensity of magnetization and on hysteresis,[1] on electrical resistance[2] and on magnetostriction[3] in permalloy has led to results of importance in the theories of ferromagnetism. It seemed that a corresponding investigation of the effect of tension on the change of thermoelectromotive force produced by a longitudinal magnetic field, might be of interest in connection with the theories of thermoelectricity.

Experimental Method

The specimens to be studied were in the form of wires 1 mm in diameter and 5 cm long, supplied to us through the kindness of L. W. McKeehan of the Bell Telephone Laboratories, Inc. Three different compositions of wires were available, viz. 78, 81 and 84 percent nickel, with the remaining part iron. These specimens were originally in the form of hard-drawn wires. Later they were annealed in a vacuum at about 1000°C for two hours and then allowed to cool gradually to room temperature in about three hours. After this heat treatment they were kept straight and free from strain of any kind.

[1] O. E. Buckley and L. W. McKeehan, Phys. Rev. **26**, 261 (1925).
[2] H. D. Arnold and L. W. McKeehan, Phys. Rev. **23**, 114 (1924).
[3] L. W. McKeehan and P. P. Cioffi, Phys. Rev. **28**, 146 (1926).

The longitudinal magnetic field was applied by means of a solenoid 40 cm in length in which the specimen was suspended axially. This solenoid was kept in a vertical position and the vertical component of the earth's magnetic field was neutralized by means of an auxiliary solenoid wound around the outside of the primary solenoid. The proper value of the current in the auxiliary solenoid just necessary to neutralize the vertical component of the earth's magnetic field was determined experimentally by means of a small earth inductor placed inside the solenoid. Throughout the subsequent experiments a current of this amount was maintained in the auxiliary solenoid. The wire to be studied was suspended from the upper end of the solenoid and provision was made at the lower end for applying tension by adding weights to a scale pan hanging from the lower end of the wire.

The upper end of the specimen terminated in a small cylindrical vessel containing a mixture of ice and water. The lower end terminated in a similar vessel containing steam at atmospheric pressure. Hence a difference of temperature of 100°C was maintained between the ends of the wire which were soldered to fine copper wires and thus formed thermal junctions kept at 0° or 100°C. The copper wires from the thermal junctions led to a White double potentiometer. By means of this potentiometer the thermoelectromotive forces arising from the couple were balanced as nearly as possible. The change of thermoelectromotive force due to a longitudinal magnetic field was determined by noting the deflection of a Leeds and Northrup galvanometer of the d'Arsonval type of known sensitivity. The magnetic fields which were nearly uniform over the center of the solenoid were determined in the usual manner from the number of turns of wire on the solenoid and the current in it.

The chief source of error was the variation of the temperature of the thermal junctions due to small variations in the temperature of mixtures of ice and water or to like variations in the temperature of the hot junction which was immersed in steam. The variations of the temperature of the mixture of ice and water were reduced to a minimum by keeping the amount of ice and water in the mixture as nearly as possible constant. The variations in the temperature of the hot junction which were gradual, were due to variations in barometric pressure and in the pressure of the steam inside the containing vessel. Errors from this source were largely eliminated by observing the zero portion of the galvanometer before and after each observation on the change of thermoelectromotive force.

Results

The results are shown in the form of curves in which the fractional change of the thermoelectromotive force has been plotted against the magnetic field parallel to the axis of the wire. In these figures the curves marked "original" were taken before the specimen was annealed. The other curves were taken after the specimen had been annealed. The tensions applied to the wire are indicated on each of the curves. These tensions are expressed in kg per mm^2. The change of thermoelectromotive force produced by the

magnetic field is a decrease. Fig. 1 shows the results for the wire containing 78 percent nickel; Fig. 2 for the wire containing 81 percent nickel and Fig. 3 for the wire containing 84 percent nickel.

In the case of the wire containing 78 percent nickel the value of $\Delta E/E$ before annealing increases from zero to a maximal value of about 8×10^{-3} as H increases from zero to about 250 gauss. After annealing the curve

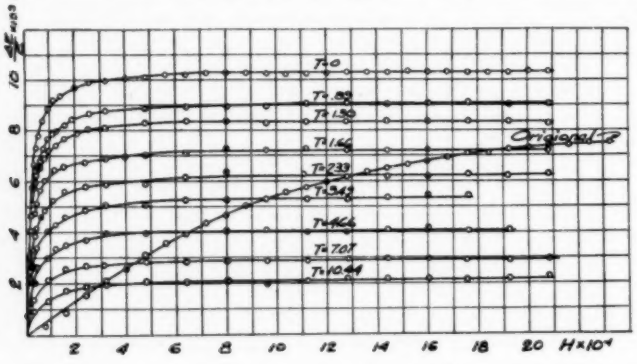

Fig. 1. Decrease of thermoelectromotive force in permalloy containing 78 percent nickel, under the combined action of tension and a longitudinal magnetic field.

(marked $T=0$) is of the same general shape as before but $\Delta E/E$ rises to a new maximal value of 10.3×10^{-3} as the field is increased to 60 gauss and remains constant at this value as H is increased to 200 gauss. In this case the value of $\Delta E/E$ increases very rapidly as H is increased from zero to 10 gauss. The application of tension leaves the form of the curve unchanged but decreases the maximal value of $\Delta E/E$ so that for a load of 10.46 kg per

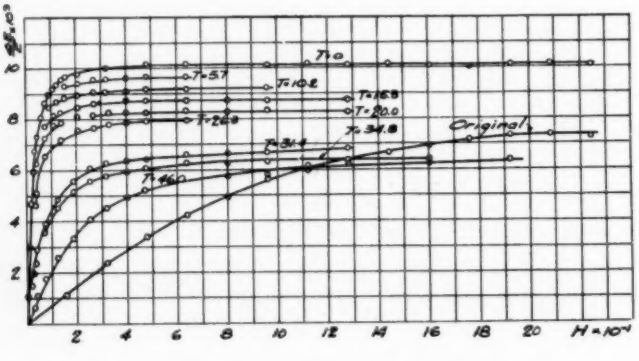

Fig. 2. Decrease of thermoelectromotive force in permalloy containing 81 percent nickel, under combined action of tension and a longitudinal magnetic field.

mm² this value of $\Delta E/E$ is 2×10^{-3} instead of 8×10^{-3} as it is for zero load. The maximal values of $\Delta E/E$ for different loads have been plotted against the load in Fig. 4. It is noted that it decreases progressively as the load is increased, approaching some limiting value as the load is indefinitely increased.

In Fig. 2, is given a corresponding set of curves showing $\Delta E/E$ as a function of the magnetic field for the wire containing 81 percent nickel. The effect of tension in this case is much less than in the case of the alloy containing 78 percent nickel. As in the former case an increase in load

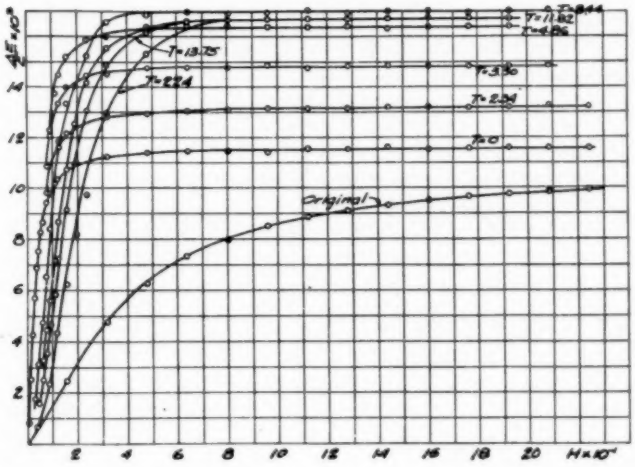

Fig. 3. Decrease of thermoelectromotive force in permalloy containing 84 percent nickel, under combined action of tension and a longitudinal magnetic field.

causes a decrease in the corresponding maximal value of $\Delta E/E$. The curve (Fig. 4) giving these values of $\Delta E/E$ as a function of the applied tension shows that in this case there is almost a linear relation between the load and the maximal value of $\Delta E/E$.

In the case of the wire containing 84 percent nickel the curve showing $\Delta E/E$ as a function of H, before the wire was annealed as well as the curve

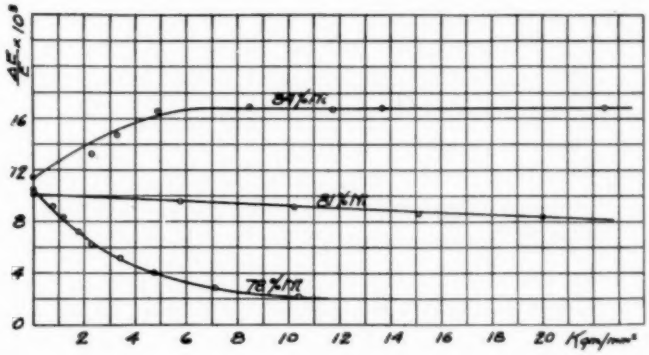

Fig. 4. The relation between the maximal change of thermoelectromotive force and tension for permalloys containing 78, 81 and 84 percent nickel.

after the wire was annealed, has the same form as the corresponding curves for the other two wires. The largest value of $\Delta E/E$ for the annealed wire without tension is 11.6×10^{-3}, which is larger than the corresponding value of other specimens. The application of tension to the alloy causes the value

of $\Delta E/E$ to decrease slightly for low magnetic fields but produces an increase in $\Delta E/E$ for magnetic fields greater than about 8 gauss. For larger magnetic fields the curves rise to successively larger maximal values until the tension is about 7 kg per mm^2. For tensions greater than this value there is no further increase in the maximal value of $\Delta E/E$. The relation between the value of $\Delta E/E$ for large magnetic fields and the tension applied to the wire is seen in Fig. 4. These curves show that this alloy has a tendency to behave like pure nickel where the application of tension decreases the effect of the magnetic field for small values of the field and increases its effect for large values of the field.

Discussion of Results

McKeehan and Cioffi[3] have shown that in an alloy containing 84 percent nickel the effect of tension is to increase the contraction for a particular longitudinal magnetic field. On the other hand there is an increase in length due to the magnetic field in the case of an alloy containing 74 percent nickel and this expansion for a particular field is less when the wire is under tension. For some intermediate value of the percent of nickel in the alloy the change of length due to the magnetic field is zero and such an alloy is relatively insensitive to tension. There is thus a reversal of the sign of the change of length and the sign of its variation due to tension. Similarly in a high nickel-permalloy tension decreases the intensity of magnetization for low magnetic fields but in a low nickel-permalloy tension increases the intensity of magnetization. In a permalloy containing 81 percent nickel the intensity of magnetization is relatively indifferent to tension. In each case the saturation value of the intensity of magnetization is quite independent of the tension. From Fig. 4. it is evident that tension produces a change in the thermoelectric behavior of the alloy containing 84 percent nickel which is opposite to the change observed in an alloy containing 78 percent nickel.

It thus appears that in a permalloy containing 84 percent nickel tension decreases the intensity of magnetization for low magnetic fields but increases the magnetostrictive contraction and the change of thermoelectromotive force produced by a longitudinal magnetic field. On the other hand in low-nickel permalloys tension increases the intensity of magnetization for low magnetic fields but decreases the magnetostrictive expansion and the change of thermoelectromotive force due to a longitudinal magnetic field. This parallelism between change of length and change of thermoelectromotive force has already been pointed out.[4] If magnetostrictions in these alloys can be interpreted in terms of atomic magnetostrictions of unlike signs,[5] it would seem that these same atomic magnetostrictions control the changes in the thermoelectromotive forces by a longitudinal magnetic field.

Mendenhall Laboratory,
Ohio State University.
November 22, 1928.

[4] A. W. Smith, Phys. Rev. **19**, 287 (1922).
[5] L. W. McKeehan, Phys. Rev. **28**, 158 (1926).

ON THE NATURE OF THE IONS IN AIR

By Henry A. Erikson

Abstract

Production and ageing of the initial positive ion in dried air and nitrogen. Effect of water vapor.—Results are given showing the production and ageing of the initial positive ion in dried air and dried nitrogen. Results are also given showing that when the final positive air ion of mobility 1.36 is passed into moist air the final ions disappear and a swifter 1.87 ion appears. Results are also given showing that these in turn change back into a 1.36 ion. The interpretation given of the above is that a neutral H_2O molecule gives up an electron to the final 1.36 two molecule positive ion thus giving a one molecule positive ion which has a higher mobility. This H_2O^+ ion ages by attaching itself to another molecule forming a slower 1.36 ion. The article closes with a statement of the reasons for the author's view that the initial and final positive ions are respectively one and two molecules large.

IN EARLIER papers[1] results have been published which indicate that an H_2O molecule transfers an electron to the final positive air ion (mobility 1.36 cm/sec per volt/cm) thus forming an H_2O^+ ion which has the same mobility as the initial positive or the negative air ions namely 1.87 cm/sec per volt/cm.

In this paper are given the results of a closer examination of this transition. A diagram of the apparatus is given in Fig. 1. *A* and *B* are two brass

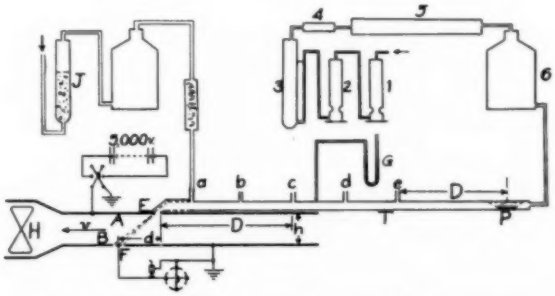

Fig. 1. Diagram showing arrangement of apparatus.

plates which form the top and bottom of a tube about 70 cm long and of rectangular cross-section. The distance between the plates *A* and *B* is 3.5 cm. Air from the room passes through the tube *AB* as a result of the action of a fan *H*, 12 cm in diameter, and driven at a speed of 5000 R.P.M. by a synchronous motor connected by a silent link-belt to a cream-separator worm. By this means an air speed of about 3500 cm/sec is obtained.

The ions are produced by placing a polonium plate at *P* in the auxiliary tube *PE*, Fig. 1 (100 cm long and 4 cm in diameter). The air passes from *P* to *E* carrying the ions with it. The air velocity in this auxiliary tube was

[1] Erikson, Phys. Rev. **30**, 344 (1927); **31**, 311 (1928); **32**, 791 (1928).

about 165 cm/sec. At E the ions pass into the main stream. Plate A was kept at a potential of about 5000 volts with reference to B which is connected to earth. In case A is positive with respect to B, the positive ions are driven across the air stream to the plate B. Because of the motion of the air they are also carried down-stream a distance d. When the electrode F is at the proper down-stream distance an ionic current is obtained which is registered by the electrometer. By plotting the currents against the distances d the ionic spectrum is obtained, the distance d for the maximum of which is proportional to the reciprocal of the ionic mobility in accordance with the relation

$$k = h^2 v / Vd$$

where h is the distance between the plates A and B, V their difference of potential, v the speed of the air, and k the mobility of the ions.

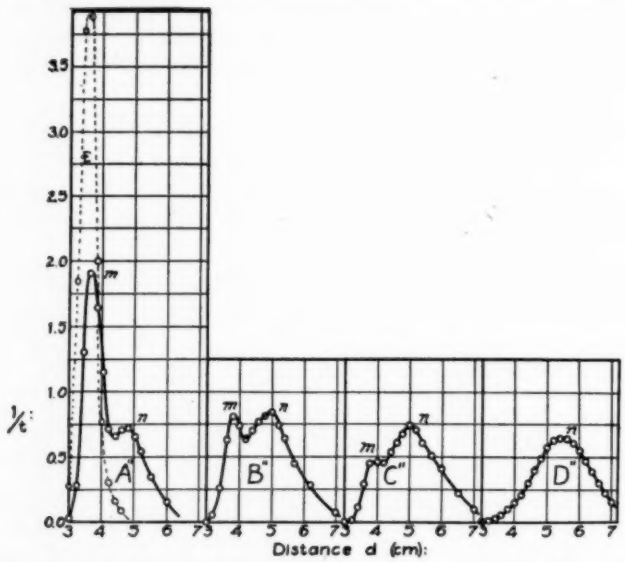

Fig. 2. Curves showing change with age of initial positive ion into final ion in dried air.

As the effect of moisture is quite marked, it is necessary to dry the air which passes through the auxiliary tube in which the ions are produced. In this work the air passed through the calcium chloride towers 1 and 2. It was then bubbled through a sulphuric acid column 3. After passing through glass wool in 4, it passed through a tube 5, 6 cm diameter and 1.2 meters long, containing P_2O_5 and glass wool. From this tube it passed into the glass chamber 6 and from there into the auxiliary tube.

In order to show what ions are formed in air dried in this manner the following observations were made. In Fig. 2, curve A'' is for the positive ion and was obtained when the polonium plate was placed at a. In this case the ions are obtained very soon after their formation. The maximum m is for the initial positive ion of mobility 1.87, the same as that of the

negative ion shown by the dotted curve *E*. Maximum *n* is for the final positive ion, mobility 1.36. Curve *B''*, Fig. 2, was obtained when the polonium was at *b*, thus giving ions a little older. It is seen how the final ion *n* is formed at the expense of the initial ions *m*. Curve *C''*, Fig. 2, was obtained when the polonium was at *c*. Practically all of the initial ions *m* have changed over to the final 1.36 ion *n*.

Curve *D''*, Fig. 2, was obtained with the polonium plate sufficiently far up stream, distance *D*, so that all the initial 1.87 ions have had time to change over. On the writer's view the initial 1.87 ion is a single molecule which has lost an electron in the ionizing process. This initial positive one molecule ion shares an electron with a neutral molecule, thus forming the final positive 1.36 ion which is therefore an ion complex two molecules large. It is this transition which is observed above.

Ions Produced in Dried Nitrogen

In order to reduce still further the chance of being misled it was decided to use nitrogen. The nitrogen was procured from the Kansas City Oxygen

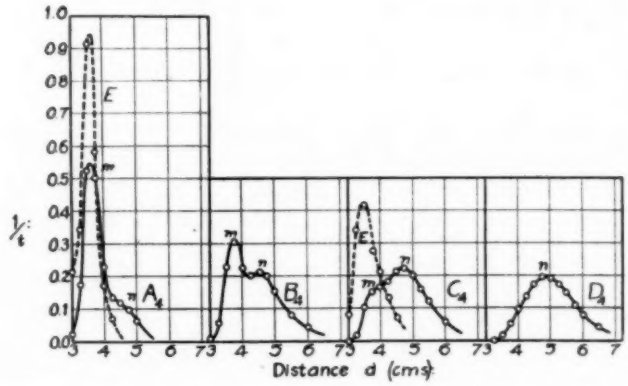

Fig. 3. Curves showing change with age of initial positive ion into final ion in dried nitrogen.

Gas Company. This nitrogen according to the Company's test has a purity of 99.7 percent or better. The gas was delivered in the usual commercial cylinders at a pressure of 1500 lbs/sq. in. The gas in the filling container is saturated. The nitrogen in the cylinders delivered is therefore somewhat below saturation.

In order to dry the nitrogen a cylinder of the same size was opened and 0.7 lb. of phosphorous pentoxide was introduced. The cylinder was then evacuated after which it was connected to the supply cylinder and the pressure allowed to equalize. The cylinder containing the nitrogen and the P_2O_5 was then allowed to stand for one week. The nitrogen was then passed directly into the auxiliary tube at *P*. The stream being adjusted by means of the reducing valve so that the surfaces of the H_2SO_4 in the gauge *G* were on the same level thus securing atmospheric pressure in the auxiliary tube.

Fig. 3 gives the results obtained. Curve A_4 is for the positive ion and was obtained with the polonium close to E, Fig. 1, all the side tubes being closed. This shows that practically all the ions are initial 1.87 ions. A trace of the final 1.36 ion is seen at n. Curve E is for the negative ion. Curve B_4 was obtained with the polonium moved up stream to b, Fig. 1, the nitrogen used having been dried for 24 hours instead of one week as in A_4. Here it is seen that more of the initial ions m have had time to change over into the final ions n.

Curve C_4 was obtained with the polonium at c, Fig. 1, the nitrogen having been dried for 24 hours. Here the initial ions m are practically gone. Curve E is for the negative ion and shows that it is unaffected. Curve D_4 was obtained with the polonium at e, the nitrogen having been dried for 24 hours. Here it is seen that all the ions are final 1.36 ions.

The conclusion from the above is that the formation of the initial ion and its transition into the final ion is a characteristic process in both air and nitrogen.

The Effect of H_2O on the Final Ion

It is seen above that when the polonium is placed up stream a distance D, all the initial ions have had time to change into the final ion. In order to examine the effect of H_2O, side tubes a, b, c, d, e were inserted in the

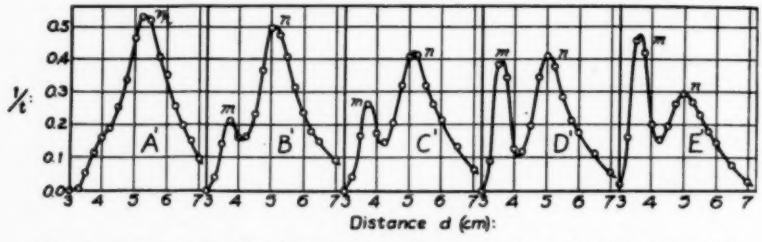

Fig. 4. Curves showing the increase in the number of initial ions with increase in amount of moisture.

auxiliary tube EP, and the polonium was placed a distance equal to D on the up stream side of the side tube e. Only the final positive ions are therefore present when they reach the tube e.

Air which had bubbled through water in the tower J, Fig. 1, was passed into the auxiliary tube at the points a, b, etc. In Fig. 4 are shown the results obtained when the moist air was admitted through the side tube a only. Curve A' was obtained with no moist air admitted. The air passing through the auxiliary tube EP, Fig. 1, was dried in this case by passing through two calcium chloride towers then through a glass tube 8 cm in diameter and 1.2 meters long containing glass wool and P_2O_5, then through two similar tubes in parallel, also containing P_2O_5 and glass wool. Curve A' shows that the positive ions present are the final 1.36 ions, n.

A small amount of moist air was then admitted through the side tube a, and the curve B', Fig. 4, was obtained. Here it is seen that the initial 1.87

ion, *m*, is appearing. Curve *C'* was obtained when more moist air was admitted at *a*. A greater number of initial ions *m* are present and less of the final. Curve *D'* was obtained with more moist air admitted at *a* and curve *E'* with still an additional amount. It is thus seen, as reported earlier, that the addition of water causes the transition of the final 1.36 ion into the initial 1.87 ion.

The writer's view is that a neutral H_2O molecule, having an ionization potential of about 13, gives up an electron to the final two-molecule 1.36 positive ion which, if it is an air ion, has an ionizing potential of the order of 16. A one-molecule positive 1.87 H_2O ion is thus formed, the 1.36 ion being neutralized.

Fig. 5 shows the results obtained with conditions the same as for Fig. 4. Here, however, a stream of constant moisture was passed consecutively through the side tubes. Curve *A* is for air dried as described in the case of air above, and with no moist air entering. Only the final ion *n* is present. Curve *B* was obtained when the moist air was admitted through the side

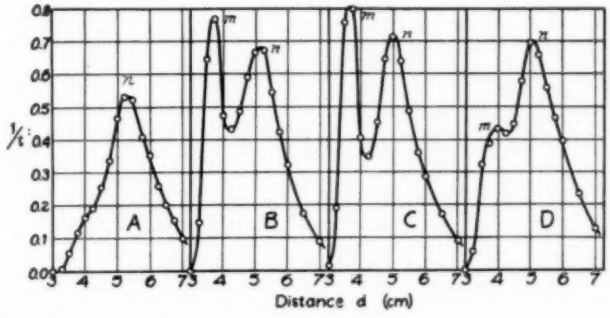

Fig. 5. Curves showing the increase, then decrease in number of initial positive ions with time in moist air.

tube *a*. It is here seen that the initial 1.87 ion *m* has formed, whereas without the moisture only the final positive ion *n* is present. Curve *C* was obtained when the moist air was admitted through the side tube *c*. It is here seen that there has been no appreciable increase in the number of initial 1.87 ions. The reason for this is that the initial 1.87 water ion formed is ageing, that is, it is attaching itself to neutral molecules and is thus again forming a final 1.36 ion. Curve *D* was obtained when the moist air was admitted through the side tube *e*. Here it is seen that the initial 1.87 water ions have quite completely changed into the 1.36 ions *n*. It is thus evident that the 1.87 positive ion formed due to the action of water attaches itself to another molecule. A point of interest here is that a higher resolving power is obtained than in the case of the corresponding air ions. This would mean that water ions are more stable. These results also indicate that the final ion represented by curve *A* is not a water ion. When the ion *n*, curve *D*, is formed its mobility should be independent of the moisture content. When

Tyndall, Starr and Powell[2] found that additional moisture did not alter the mobility of the final ion in a closed vessel they were no doubt measuring in terms of the final water ion.

In two interesting articles[2,3] which appeared recently it is found that in closed vessels the initial ions do not appear. Mahoney finds, however, that the initial ion is present in a closed vessel when moist air is used and that this initial ion changes with age into the final ion. Tyndall, Starr and Powell also find only a slight indication of the presence of the intial ion in a closed vessel and suggest that the reason may be that something very favorable to the rapid transmission of the initial ion accumulates in a closed vessel. They suggest that it may be ozone formed by the ionizing rays.

Tyndall, Grindley and Sheppard[4] find that in using a blast method like the above the initial ion appears normally as found by the writer. In introducing ozone they find that the formation of the final ion is enhanced.

The experience of the writer leads him to favor this view. For example, when room air which has been heavily ionized by means of beta-rays, but from which the ions have been removed by means of a field, is passed through the auxiliary tube, Fig. 1, where it is again ionized by the polonium, a greater proportion of final ions is obtained. In a closed vessel these products accumulate and an increased effect may be expected.

Since the results given in this paper were obtained, the writer has remodeled the apparatus so that the air through the auxiliary tube, after passing through $CaCl_2$ and P_2O_5, passes through copper coils immersed in liquid air, care being taken to have the air also pass through glass wool while cold. It is then found that only the initial ion is obtained at short age and also that the rate of transition of the initial into the final ion is very greatly reduced. It is also found that passing the air through $CaCl_2$ and P_2O_5 only, without the liquid air cooling, favors greatly the formation of the final ion. When air which has bubbled through H_2SO_4 is used the negative ion is also affected. These results will appear in a later publication.

Discussion of Results

The question of interest is:—Are the above ions clusters of several molecules or are they of a simple one or two-molecule structure? It is accepted that the ionizing process consists in an electron leaving a molecule under the action of the ionizing ray. On the basis of no appreciable dissociation by the rays one is forced to assume that the positive ion formed as a consequence of the ionizing process is initially one molecule large provided of course that the medium ionized is in the molecular state. In the permanent gases such as nitrogen, oxygen, CO_2, argon, etc., at normal temperature, this is conceded to be the state. There is furthermore evidence that in the ionizing process only one electron is emitted from each body ionized. To this helium seems to be a slight exception.

[2] Tyndall, Starr and Powell, Proc. Roy. Soc. **A121**, 172 (1928).
[3] Mahoney, Phys. Rev. **33**, 217 (1929).
[4] Tyndall, Grindley and Sheppard, Proc. Roy. Soc. **A121**, 185 (1928).

The conclusion therefore is inevitable that the initial positive ion formed in the permanent gases is one molecule large. There is evidence that the electron emitted in the ionizing process remains free but a very short time. The only possibility the electron has for terminating its free state is initially to attach itself to a neutral molecule of the medium. It is thus seen that initially, one is forced to think in terms of a one molecule positive ion and a one molecule negative ion.

By using the blast method described above, the writer[5] was able, as is also shown above, to evaluate the ions very soon after their formation in air. It was then found that in air the positive ion has the same mobility as the negative ion. The value of this common mobility is 1.87 cm/sec per volt/cm. This value of 1.87 is the highest value observed in air at normal temperature and pressure neglecting small variations depending upon the degree of purity of the medium. Since the mobility value 1.87 is the same for both the initial positive and negative ions they must have the same charge and the same complexity of structure as to molecular grouping. The most obvious conclusion therefore is that these two 1.87 bodies are the initial one molecule positive and negative ions referred to above. Were they clusters of several molecules a time interval for their formation would be necessary which should be detectable in the measurements. No evidence of this has been obtained. Furthermore were these two 1.87 ions clusters of several molecules it is not likely that the equilibrium value for the mobility would be the same for the positive as for the negative since their natures are different. The positive is deficient in electrons and therefore has an electron affinity, the negative on the other hand has an excess of electrons and is surrounded by neutral molecules which have their electron affinity already satisfied. In this reasoning one does not include gases of the character of chlorine which have an electron affinity. As is observed above and as was observed by the writer several years ago, the initial positive 1.87 ion soon changes into an ion of mobility 1.36 cm/sec per volt/cm which is the final positive ion and which is a fairly stable structure. It is possible to obtain a resolving power sufficiently high so that the final positive ion may be separated from the initial ion. Fig. 6 shows what is possible in the way of resolution. The maximum m is for the initial (1.87) ion and the maximum n is for the final (1.36) ion. In this process of separation there is no evidence of intermediate ions. As seen above in Fig. 2 it is possible by increasing the time to observe the formation of the final ions at the expense of the initial ions. If the initial and the final positive ions were clusters of several molecules the above clear cut observations would not be thinkable. Intermediate bodies would be inevitable in the process of formation which would preclude a clear cut resolution such as is found possible. The conclusion seems inevitable that the 1.36 ion is due to the initial one molecule, 1.87 ion,

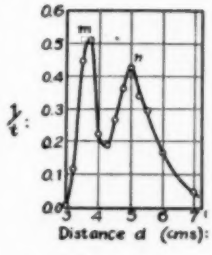

Fig. 6. Curve showing degree of possible separation between initial and final positive ions.

[5] Erikson, Phys. Rev. **20**, 117 (1922).

attaching itself to a neutral molecule thus forming a two molecule ion complex the characteristic mobility of which is 1.36. If, furthermore, the two positive ions are clusters it is difficult to see why these two would be stable and other groupings unstable.

It is seen above that when H_2O is added to the air the final 1.36 ion disappears and a 1.87 ion is formed. As stated above the writer believes that the H_2O molecule having a lower ionizing potential gives up an electron to the final 1.36 ion thus neutralizing it and giving in its place a one molecule H_2O positive ion which since it is one molecule large and carries a single charge has the mobility 1.87, the same as the negative ion, and which is characteristic of a one molecule ion. Were the ions clusters it is hardly to be expected that the 1.87 value would result from an alteration of this character.

In earlier papers it was shown that the same two characteristic values are obtained when argon, CO_2 and hydrogen are passed through the auxiliary tube.

The values 1.87 and 1.36 are so different and so distinctive that it is difficult to avoid the conclusion that they represent the first and second steps in molecular aggregation. In other words that the value 1.87 is characteristic of a one molecule ion and the value 1.36 characteristic of a two molecule ion.

Air, argon, CO_2, hydrogen and actinium, thorium and radium active deposits have ions of comparable mobilities in air. This means that the mobility is practically independent of the mass of the ion. Apparently the mobility depends almost wholly upon the charge carried by the ion, the resistance to motion being determined by the polarizing action on the adjacent molecules of the medium. Apparently also the mobility is independent of the structure of the molecule, for example atomic argon and CO_2.

As soon, however, as an artificial attachment between two or more molecules takes place the mobility changes. It seems necessary to distinguish in mobility work between an artificial grouping forming complexes and the natural atomic grouping in the molecule. For example, suppose two molecules *a* and *b*, one of which has a positive charge, become attached to each other. They form a complex of two molecules which has a mobility value which is less than 1.87, the characteristic value being 1.36. If then the *n* atoms in *a* and the *n* atoms in *b* rearrange themselves so as to form a natural one molecule structure, the mobility immediately changes to 1.87, the value which is characteristic of a one molecule ion.

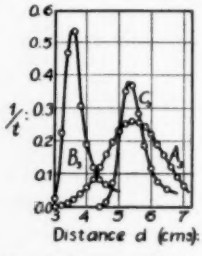

Fig. 7. Curves showing that the final positive ion curve is wider than the negative ion curve for the same diagonal path.

The final 1.36 positive ion is not a completely stable body. The widths of the curves for the final positive ions is indicative of this. That the greater width of the final positive ion curve is not due to the greater obliquity at which the ions come to the electrode is shown by the curves in Fig. 7. Curve A_3 is for the final positive 1.36 ions. Curve B_3 is for the negative ion, mobility 1.87, obtained at the same voltage and air velocity as Curve A_3.

Curve C_3 is for the negative ion when the voltage was reduced so that the negative maximum comes at the same down stream distance as the maximum of the final positive ion.

It is thus seen that the width of the curve C_3 is not comparable to that of A_3. This must mean that the final 1.36 positive ion is not highly stable. In passing between the plates AB, Fig. 1, it may simplify back to a one molecule initial ion thus reaching plate B farther up stream or the final 1.36 ion may attach itself temporarily to a third molecule and therefore pass farther down stream. Both of these effects cause a widening of the curve.

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A THEORY OF AURORAS AND MAGNETIC STORMS*

By H. B. Maris and E. O. Hulburt

Abstract

The physics of the atmosphere of the earth under a quiet sun is discussed in detail. The daytime temperatures above 100 km increase with the height to roughly 1000°K at a 400 km level; new tables of the molecular density of the atmosphere to great heights are given. In the region above 450 km, where the molecular free paths are very long, a portion of the highly absorbed ultra-violet light of the sun is converted into kinetic energy, by processes of atomic excitation and ionic recombination, and produces 10^8 atoms cm^{-2} sec^{-1} which fly out from the earth with velocities of 10 km sec^{-1} or more. The atoms attain levels of 30000 to 50000 km in 3 hours and are then ionized by the ultra-violet sunlight. The ion pairs thus formed spiral about the lines of force of the earth's magnetic field and a majority are guided to the polar latitudes. They fall into a zone roughly 25° from the magnetic poles and give rise to the *auroras* there; this is the observed zone of maximum auroral frequency. It takes the ions 9 hours to travel from the equator to the poles, and therefore the aurora occurs more often in the early hours of the night than in the later hours, as is observed. The fact that short wireless waves traverse polar regions supports the view that the ionization is due to the ion influx from lower latitudes; for the sunlight is too weak to make many ions there. It is assumed that the sun, when active, emits a sudden (1/2 hour) blast of ultra-violet light. For example, if 1/10000 part of the solar surface, normally at a temperature of 6000°, were removed and there were exposed the black-body radiations at 30000°, the solar constant would be increased by 1 percent and the ultra-violet energy, λ500 to 1000A, by 10^5. This ultra-violet energy, completely absorbed in the high lying (200 km) atmospheric gaseous layers, blasts out these layers to produce ions up to 40000 km. Due to gravity and the earth's magnetic field the first effect of the high flying ions is to produce a sudden current, 10^6 amperes, in planes parallel to the equator, which causes a magnetic field 10^{-3} gauss simultaneously over the whole earth, as is observed in the first phase of the world-wide magnetic storms. Numbers of ions descend to the zones 23° from the magnetic poles and form there diamagnetic concentrations of considerable intensity (also give rise to the auroras). On the assumption that the blast of ultra-violet light does not die away abruptly but continues with lessening intensity for a day or so, the diamagnetic concentrations wax with the day and wane with the night. The changes in the earth's magnetic field caused by this diamagnetism are found to agree in nearly every detail with the observed complicated diurnal storm variations in the three magnetic field components at all latitudes.

1. *INTRODUCTION.* The temperatures and pressures of the gases of the atmosphere up to heights of 200 km above the surface of the earth and the ionization in these regions caused by the ultra-violet light of the sun have been discussed in two recent papers [1,2]. The ionization was found to be in keeping with that inferred from the behavior of wireless waves; the increase and decrease in the ionization with day and night was shown[3] to give rise to magnetic effects in complete agreement with the observed diurnal var-

* Published by permission of the Navy Department.

[1] Maris, Nature, **120**, 839 (1927); Ter. Mag. and Atmos. Elec. **33**, December (1928).

[2] Hulburt, Phys. Rev. **31**, 1018 (1928).

[3] Gunn, Phys. Rev. **32**, 133 (1928).

iations in terrestrial magnetism. It has been the purpose of the present paper to examine into the physics of the atmosphere in regions above the 200 km levels, regions extending to 50000 km from the surface of the earth. It may be stated in advance that in this outlying domain, which verges into interplanetary space, are found ions and electrons ejected from the terrestrial atmosphere by the ultra-violet light of the sun. The effects of these high flying electrified particles afford a comprehensive explanation of the characteristics of the aurora and of the complicated variations in the magnetic field of the earth at all latitudes during a magnetic storm.

Sections 2 to 9 deal with the atmosphere under conditions of solar quiet, i.e. no terrestrial auroras or magnetic storms, sections 10 to 16 deal with the case of an active sun.

2. *The atmosphere to 500 km; quiet sun.* Earlier calculations [4,5] of the pressures of the constituent gases of the atmosphere were based on the assumptions of a constant temperature, 222° at great heights, of complete diffusion below a level, known as the "diffusion level," which was taken without justification to be 0 to 50 km, and of gravity equilibrium above this level. No differences between night and day or winter and summer were recognized. It was clearly realized that the assumptions were at best only approximate and would be expected to break down entirely at great heights. The whole matter was gone over again from the beginning several years ago[1] and the diffusion level was shown to be at about 160 km for a summer day, and at 130 km at night, by considering the time it would take a thoroughly mixed atmosphere to settle out and reach gravity equilibrium. The diffusion level is a little different for each gas. The heating of the atmosphere by the sunlight was calculated and complete tables[1] of the molecular densities were given approximately valid to about 150 km levels.[6]

For the purposes of the present discussion the tables have been extended to greater heights. The night-time values of the temperature T°K and the molecular density n, i.e. the total number of molecules or atoms of all sorts per cm^3, are given in columns 2 and 3, Table I; these are the same as in the earlier tables.[1] The daytime values, columns 4 and 5, Table I, were gotten by calculating the heating by the sun step by step in each level of the atmosphere, using the ultra-violet and infra-red absorption coefficients of ozone and assuming the proportion of ozone to remain constant above 60 km, on the idea that the ozone is created by the sunlight at each level. The sun was assumed to be quiet, i.e. no terrestrial auroras or magnetic storms, and the solar spectral energy to be that of a black body at 6,000°K. Because of the unequal balance at cold temperatures between the solar energy absorbed in the ultra-violet by the atmospheric gases and the energy re-emitted in the infra-red by the gases, the daytime (i.e., the sun directly overhead) temperatures above 50 km increased with the height as shown in column

[4] Chapman and Milne, Roy. Meteor. Soc., Quarterly Jr. **46**, 357 (1920).

[5] Humphreys, "Physics of the Air," (1920).

[6] Gowan, Proc. Roy. Soc. **128**, 655 (1928), has recently considered the heating in much the same way, neglecting day and night differences.

4 of the table. The complete tables of the partial pressures of the atmospheric gases and the details of the calculations are too long to give here. The daytime diffusion level is at about 250 km, which is a little higher than before[1] because of the greater temperatures at the greater heights. An estimate of the temperature of the upper atmosphere may be made from the width of the non polar aurora green line λ5577.35A in the night sky, which was observed by Babcock[7] to be not more than 0.035A wide. With

TABLE I. *Atmospheric temperatures and densities at various altitudes.*

	Quiet Sun				Active Sun	
Height	night		day		day	
	T	n	T	n	T	n
0 km	288°K	2.56×10^{19}	288°K	2.56×10^{19}	288°K	2.56×10^{19}
10	228	8.26×10^{18}	228	8.26×10^{18}	228	8.26×10^{18}
20	223	1.91×10^{18}	228	1.90×10^{18}	230	1.89×10^{18}
40	232	9.37×10^{16}	280	8.22×10^{16}	390	5.90×10^{16}
80	232	2.81×10^{14}	560	1.23×10^{15}	1120	2.10×10^{15}
100	232	1.59×10^{13}	620	3.49×10^{14}	1220	9.23×10^{14}
150	232	1.60×10^{10}	1000	2.15×10^{13}	1500	1.64×10^{14}
200	232	1.78×10^{7}	1000	3.97×10^{12}	1500	4.55×10^{13}
250	232	6.98×10^{5}	1000	7.98×10^{11}	1500	1.47×10^{13}
300	232	2.78×10^{5}	1000	1.66×10^{11}	1500	4.98×10^{12}
400	232	4.42×10^{4}	1000	7.40×10^{9}	1500	6.00×10^{10}
500	232	7.51×10^{3}	1000	3.66×10^{8}	1500	6.29×10^{11}
600	232	1.31×10^{3}	1000	2.08×10^{7}	1500	8.86×10^{9}
800	232	4.73×10	1000	3.68×10^{5}	1500	2.01×10^{8}
1000	232	2.07	1000	1.75×10^{5}	1500	5.90×10^{6}

this value and taking the oxygen atom[8] to be the emitting particle, the temperature calculated on the theory of Doppler broadening[9] came out to be 880°K, an upper limit. One would expect the conditions in the high atmosphere to be ideal for the Doppler broadening theory. This is higher than the night values of Table I, but serves perhaps as some justification for the general idea of high temperatures in the outer atmosphere.

At 400 km in the daytime only about 1/10,000 of the atmosphere is helium, the rest being mainly oxygen and nitrogen; above 800 km helium predominates. Following Chapman and Milne[4] it has been assumed that there is no hydrogen in the high atmosphere; at a 400 km level, however, the inclusion of hydrogen would make little change, at greater heights the effect of hydrogen would be important. The presence or absence of hydrogen can not be regarded as settled at the present time. The assumption which we have used about ozone can hardly be correct and the values in Table I can at best only be approximately true. One should consider as well the

[7] Babcock, Astrophys. J. **57**, 209 (1923).
[8] McLennan, Proc. Roy. Soc. **120**, 357 (1928).
[9] Fabry and Buisson, Jour. de Physique, **9**, 189 (1919).

other gases, such as nitrogen, helium, etc., but the light absorption coefficients (transition probabilities) are not known, and any calculations based on them would have little meaning.

3. *The atmospheric spray up to 50,000 km levels.* From Table I at 450 km $n = 1.60 \times 10^9$ in the day. The free path of a particle of diameter 10^{-8} cm is of the order 10^2 km at this height and increases rapidly with the height. Above 450 km there are 10^{16} molecules cm^{-2}; these experience 10^{11} collision per second at the 450 km level. Approximately 10^{16} molecules of diameter 10^{-8} cm will just fit into an area of 1 $cm.^2$ Therefore above 450 km there are practically no collisions and the values given in column 2 to 5, Table I, above this level, which were based on assumptions of kinetic gas equilibrium, have little meaning; they had to be worked out of course in order to reach this conclusion. The 10^{16} molecules dance up and down, receiving upward thrusts from thermal impacts below and falling back under gravity. At 1000°K the thermal velocities of a nitrogen molecule, a helium atom and a hydrogen atom are 0.9, 2.3 and 4.6 km sec^{-1}, respectively. With these velocities of projection the respective particle will reach heights of about 1000, 2000 and 5000 km above the surface of the earth. For these calculations and others, given later, see any chapter on central orbits.[10]. Therefore, omitting hydrogen, due to temperature velocities alone we may expect a fringe of 10^{16} molecules, or atoms, in a 1 cm^2 column extending from 450 km up to 2000 or 3000 km, but hardly above this.

In the high fringe of the atmosphere calculations based on kinetic theory averages begin to break down, and therefore we pass, as we should, from macroscopic to microscopic considerations and examine the behavior of individual particles. The sunlight, particularly in the wave-lengths less than 1200A, in addition to heating the atmosphere, causes excitation, dissociation and ionization of the atmospheric atoms and molecules. Neutral particles which collide with the excited ones, or with particles undergoing recombination, may receive some or all of the excitation or recombination energy in the form of kinetic energy. *It is assumed that a portion of the energy of the short wave-length ultra-violet light of the sun causes some neutral atoms or molecules to move at speeds as great as 10 km* sec^{-1}. In illustration, if a helium atom collides with another helium atom excited to 4 volts, each acquires a velocity of 10 km sec^{-1}; or a helium atom which releases by collision 2 volts excitation energy from a nitrogen or oxygen molecule acquires a velocity of 10 km sec^{-1}; about this same velocity is given to an oxygen atom which releases 13.5 volt excitation energy from an oxygen molecule, or to a nitrogen atom which collides with another nitrogen atom excited to 15 volts. Eddington[11] calls collisions of this sort "superelastic collisions," Frank[12] calls them "collisions of the second kind." Direct experimental evidence of the assumption is found in the observed fact[13] that the luminous particles in a

[10] For example, Taite and Steel, "Dynamics of a Particle," page 113 (1889).

[11] Eddington, "The Internal Constitution of the Stars," page 373 (1926).

[12] Frank and Jordan, "Anregung von Quantensprüngen durch Stösse," (1926).

[13] Russell, Dugan and Stewart, "Astronomy," 1, 441 (1926).

comet's tail ejected from the nucleus move with velocities of several kilometers per second, velocities which are recognized to be unexplainable by light pressure.

We give a quantitative turn to the assumption of the preceding paragraph and assume that, of the 10^{14} collisions which the 10^{16} molecules of a 1 cm² column of the atmospheric fringe make per second, 2×10^{6} are of a sort to give a neutral atom a velocity about 10 km sec^{-1}. There may be velocities less and greater than this, of course. Thus there are 2×10^{6} cm^{-2} sec^{-1} high speed atoms, one half of which fly downward to be lost in the atmosphere below, and the other half upward. The orbits[7] of particles projected with a velocity of 10 km sec^{-1} at angles of 1°, 22°, 45° and 60° with

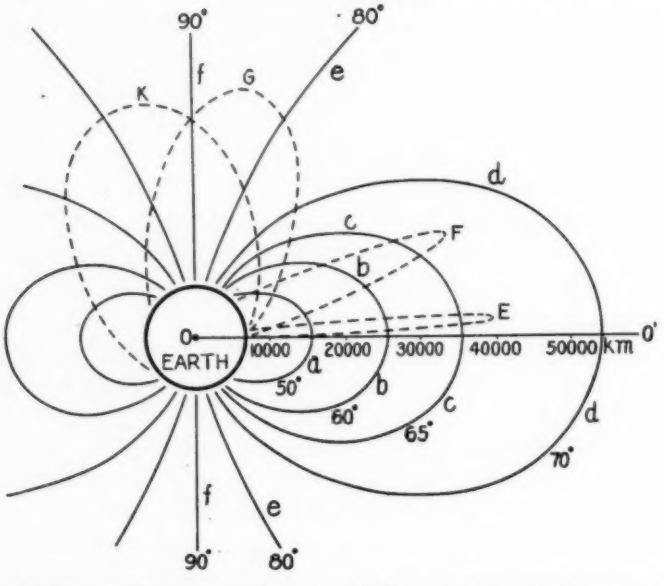

Fig. 1. Curves *aa*, *bb*, etc., are the magnetic lines of force of the magnetic field of the earth. The number near each curve is the magnetic latitude where the line touches the earth. Curves *E*, *F*, *G* and *K* are the orbits of particles projected from the earth with a velocity of 10 km sec^{-1} at angles to the vertical of 1°, 22°, 45° and 60° respectively.

the vertical are given in the dotted curves *E*, *F*, *G* and *K*, respectively, of Fig. 1. The figure is drawn to the scale marked on 00′. Particles projected vertically upwards with velocities 10 and 10.5 km sec^{-1} reach heights 45,000 and 100,000 km from the center of the earth in 3.0 and 15.4 hours, respectively. (The velocity for projection to infinity is 11.18 km sec^{-1}). Thus on the sunlit side of the earth there is a spray of atoms and molecules extending out to 50,000 km or so.

4. *Ionization of the high flying atoms and molecules by the ultra-violet light of the sun.* The high flying atoms (or molecules) are ionized by the ultraviolet sunlight in a time t sec given by the relation

$$t = w/I_0(1-e^{-\beta}), \tag{1}$$

where w is the ionization potential of the atom, β the atomic absorption coefficient and I_o the intensity of the ionizing light. A more detailed theory than the present would consider the value of β for each wave-length of the light, etc.; this is not done here. β is defined in the usual way by the equation

$$I = I_0 e^{-\beta n x}, \tag{2}$$

where I is the intensity of the light after passing through x cms of atoms, or molecules, of density n. (1) is derived from (2) by assuming that all of the absorbed energy goes to produce ionization, and by noticing that $w = t(I_o - I)$. The ionization potentials of oxygen, nitrogen and helium atoms are 13.56, 17 and 24.6 volts, respectively, corresponding to ionizing wave-lengths 912, 725 and 502A.. The total energy of the sunlight in the wave-lengths from 0 to 502A falling on the earth is 1.2×10^{-11} erg cm^{-2} sec^{-1}, from 502 to 725A is 2.1×10^{-5} erg cm^{-2} sec^{-1}, and from 725 to 912A is 1.15×10^{-2} erg cm^{-2} sec^{-1}, calculated on the assumption that the sun is a blackbody at 6000°K and taking the solar constant, i.e. the solar energy in all wave-lengths, to be 1.35×10^{6} erg cm^{-2} sec^{-1}. Approximately we take $I_o = 10^{-4}$ erg cm^{-2}, and $w = 3.1 \times 10^{-11}$ ergs corresponding to 20 volts. The value of β, which is of course Einstein's "probability of transition," is taken to be 3×10^{-11}. With these values in (1) t is 10^4 sec, or about 3 hours, and we see that the high flying atoms of velocities about 10 km sec^{-1} become ionized after reaching 40,000 to 50,000 km levels.

The values used in (1) to give $t = 10^4$ sec. are rough averages of quantities which are not known with certainty. A value of 10^{-4} for β may be rather high (reference 2, page 1026), and the value for I_o may be low, for the solar energy curve in the ultra-violet in all probability departs from the blackbody curve (reference 11, page 328) and may be rather in the nature of line emission; similarly the absorption of the far ultra-violet light in the terrestrial atmosphere is probably line absorption.

5. *The high flying ions follow the lines of force of the magnetic field of the earth.* The high flying atoms, once ionized, are caught on the magnetic lines of force of the earth. These lines are drawn in aa, bb, cc, ee, etc., Fig. 1 the numbers written at each line giving the magnetic latitude where the line touches the surface of the earth. The lines are plotted from the usual formula for a uniformly magnetized sphere,

$$r/r_0 = \cos^2 \alpha / \cos^2 \alpha_0, \tag{3}$$

where r and α are the polar coordinates of a point on the line, r_o being the distance from the centre of the earth 0 and α the angle measured from 00,′ Fig. 1. r_o and α_o are the coordinates of the point where the line crosses the surface of the earth. The strength H of the magnetic field at any point (r,α) is

$$H = M(1+3 \sin^2 \alpha)^{1/2}/r^3, \tag{4}$$

where M is the magnetic moment of the earth. In general the path of an ion moving under the influence of the earth's gravitational and magnetic fields is very complicated. It is sufficient here to discuss a simple case. The

radius ρ of the spiral which an ion of mass m, charge e, and velocity v normal to a magnetic field H, is, using throughout c.g.s electromagnetic units,

$$\rho = mv/He. \tag{5}$$

At a height of 40,000 km, H is of the order 10^{-3} gauss from (4), and for an oxygen atom moving at a velocity of 5 km sec^{-1} ρ is only 4 km from (5) for smaller velocities and lighter atoms ρ is less than 4 km. It is considered that velocities greater than 5 km sec^{-1} at these heights will be relatively rare, (a particle projected upwards with a velocity of 10.5 km sec^{-1} has a velocity of 2.7 km sec^{-1} at a height of 53,000 km) and therefore the ions formed from the high flying atoms move in a tight spiral path along the magnetic force lines, the positive ion going around in one sense and the negative electron in the opposite sense, the ion stream remaining on the whole neutral.

6. *Concentration of the ions in polar regions; the characteristics of the aurora.* In an earlier paper[14] the total energy of a strong auroral display was estimated to be roughly 10^{15} erg sec^{-1}, and a theory was outlined which attributed the energy of the aurora to arise from the recombination of ion pairs which were formed at lower sunlit latitudes and drifted to the polar regions along the magnetic field lines of the earth. In the following paragraphs the theory is developed in some detail. The important facts[15] of the aurora are that the aurora occurs more often in the early hours of the night than in the late hours, that there is no marked seasonal variation in the frequency of auroral occurrence, possibly an uncertain maximum at equinox, and that there is a zone of maximum auroral frequency at about 23° from the magnetic pole. The average number of aurora displays in a year is plotted in curve 1, Fig. 2, as ordinate against the magnetic latitude as abscissa. The maximum is at 67°; at latitudes above this the curve is dotted, for no data are given, merely the statement that in the high latitudes the aurora is less frequent.

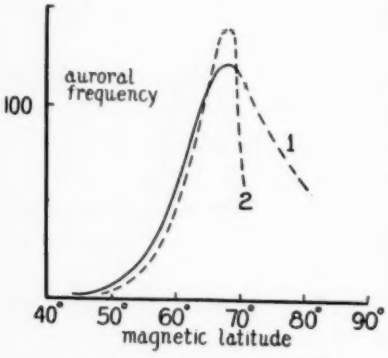

Fig. 2. Curve 1 is the average number of auroras plotted against the magnetic latitude; curve 2 is a theoretical curve of auroral frequency based on a number of assumptions.

In order to find out where the high flying ions come down to the earth and hence to determine the geographical distribution of their flux density, the distribution of velocities of ejection of the high flying neutral atoms, from which the ion pairs are formed, must be specified. This is not known—in earlier paragraphs we have merely assumed that there are some neutral atoms with velocities as great as 10 or 10.5 km sec^{-1} —but an illustrative calculation may be made on the assumption that the velocities are equally distributed among the atoms. In this case the number of atoms with a speci-

[14] Hulburt, Phys. Rev. **31**, 1038 (1928).

[15] Chree, Encyclopaedia Britannica. 13th ed., **2**, 927 (1926).

fied energy is proportional to the square root of the energy. Assuming always 3 hours for ionization an atom with velocity 10.2 km sec^{-1} is ionized at 40,000 km above the centre of the earth in the tropical or temperate zones, and upon moving up or down the magnetic line arrives at the earth at the magnetic latitude 69° (north or south). Whereas an atom with velocity 9.5 km sec^{-1} reaches its maximum height of 29,000 km in 2.4 hours, falls back to 25,000 km in 0.6 hours where it is ionized, and thence arrives at the earth at latitude 59°. A complete table was worked out for various velocities and from this, with the assumption of equal distribution of velocities among the atoms, the intensity of the ion flux was determined for each latitude. This is plotted as ordinate in curve 2, Fig. 2, in arbitrary units. If the aurora derives its energy from the ion flux, curve 2 is also a theoretical curve of aurora intensity, and hence of aurora frequency; the curve agrees roughly with the observed curve 1 up to the magnetic latitude 67°.

Above the latitude 67° the theoretical curve 2 should fall to lower values in accord with qualitative observation. It is possible that this may be due to the effect of the centrifugal force of the earth's rotation on the high flying ions. This effect, if it exists, becomes important above 40,000 km. At a distance 42,200 km from the center of the earth the centrifugal force is equal to the earrh's gravitational attractive force, as found by solving for r in the equation $MG/r^2 = r\omega^2$, where M is the mass of the earth 6×10^{27} grams, G the Newtonian constant 6.66×10^{-8} and ω the velocity of angular rotation of the earth about its axis. The calculation refers to the equatorial plane and neglects the angle between the magnetic and geographic axes. Therefore if the centrifugal force is operative ions at or above 42,200 km will rarely return to the earth. Since the line of magnetic force at this level descends to the earth at latitude 67°, few ion pairs will reach latitudes above this, only those in oblique orbits such as G, Fig. 1. This is a possible explanation of the maximum in the auroral frequency curve. If, on the other hand, the centrifugal force effect does not exist, one must have recourse to special hypotheses to explain why the aurora is less frequent at latitudes above 67°, namely, one may suppose that few ion pairs reach levels where they may be guided to the high polar zones on the idea that either the neutral particles are ionized too quickly or that they do not have sufficiently great velocities of projection. The question of the centrifugal force is discussed further in section 9. The influence of radiation pressure on the atmosphere has been neglected. Although classical calculation indicated that this effect was relatively small, it may turn out to be of importance.

It takes a 10.2 km sec^{-1} atom 3 hours to reach 40,000 km levels (and a 9.7 km sec^{-1} atom 3 hours to reach 34,000 km), and another 6 to 14 hours to fall down to the polar regions. Meanwhile the earth turns an hour or two under the flying atom; after being ionized the atom is constrained by the magnetic field to have the same angular rotation velocity as the earth. Since the ions are produced by the ultra-violet light of the sun the maximum rate of production occurs at noon. Therefore, the maximum ion flux in the polar regions occurs in the early part of the evening, 9 hours or more after noon,

just as is observed for the aurora intensity. The fact that there is no very marked seasonal variation in the aurora intensity is in keeping with the present ideas, for the theory, at least in its present rough form, indicates no marked influence upon auroral occurrence of the tilts in the geographic and magnetic axes.

Because of winds the high atmosphere is not uniform, and there may be here and there pressures of, say, nitrogen greater or less than the average. Under the solar excitation, which is also variable, one may expect fitful gusts and clouds of high flying atoms. After being ionized these descend to the auroral zones lengthening into streaks and, being touched into luminosity, form the auroral streamers. Certain groups homogeneous in velocity may descend in thin sheets to form the auroral curtains and draperies.

7. *The energy of the aurora.* In order to determine the rate of transfer of energy by the high flying ions from the sunlit lower latitudes to the auroral zone, we deal only with the ions with velocities around 10 km sec^{-1}, which attain 40,000 km levels, and assume that the number of these which move outward in a direction at an angle θ with the line joining the earth and the sun is proportional to $\cos\theta$; c.f. Lambert's law for light reflected from a diffusing surface. Practically all of the 10 km sec^{-1} atoms moving outward in directions embraced in a 90° cone, as in the orbits E, F and G, Fig. 1, are concentrated at the earth in the 65° region. These comprise 3/4 of the total number ejected in all directions, as found by a simple integration. The other 1/4 are sent out at angles less than 45°, as in orbit K, Fig. 1, and upon being ionized, eventually are scattered over the magnetic polar regions and elsewhere without marked concentration. The target area of the earth is $\pi r_0^2 = 1.3\times10^{18}$ cm^2, the radius of the earth r_0 is 6400 km; the area of the auroral zone, between magnetic latitudes 65° and 70° and longitudes 180° apart, is 2.17×10^{16} cm^2, and as there are two such zones one in the north and one in the south, the total area is 4.34×10^{16} cm^2. According to the assumption of section 4 there are 10^6 cm^{-2} sec^{-1} high flying atoms produced by the sunshine. 10^{-5} erg cm^{-2} sec^{-1} is required to give these a velocity of 10 km sec^{-1} (actually, 1.16×10^{-5} and 0.33×10^{-5} for nitrogen and helium atoms, respectively) and 3.1×10^{-5} erg sec^{-1} to ionize them at 20 volts, a total of 4.1×10^{-5} erg cm^{-2} sec^{-1}, or $4.1\times10^{-5}\times1.3\times10^{18} = 5.3\times10^{13}$ erg sec^{-1} for the sunlit hemisphere. Three fourths of this, or 4×10^{13} erg sec^{-1}, goes to the auroral zones and is available as auroral energy. This is somewhat less than 10^{15} erg sec^{-1} estimated for a strong auroral display. This is as it should be, and we have chosen the numerical estimates to give this result on the idea that there are no auroras in the intervals of solar quiescence. If the ultra-violet sunlight is increased in intensity, as in a time of solar disturbance, then the energy carried to the auroral zone is greater than usual and an auroral display results. This is discussed in section 11.

The foregoing estimates are based on the assumption that a portion of the solar energy is transferred continually into auroral energy. This may not actually be the case, for it may be that the polar energy is stored up for a time in the atmosphere until it finds, or gives rise to, conditions suitable for

its release. On the whole this discussion can only be regarded as the preliminary framework of a more complete development. Such a development will require, among other things, complete knowledge of the energy levels, metastable states, and transition probabilities of the atmospheric atoms and molecules, as well as of the exact atomic processes which give rise to the aurora light.

8. *The connection between the present calculations and the theory of the Kennelly-Heaviside layer.* The ionization in the 100 to 200 km levels, known as the Kennelly-Heaviside layer (wireless wave propagation phenomena depend for the most part on this ionization) has been shown[2] to be due to the solar ultra-violet light, an energy flux of 4.5×10^{-3} erg cm^{-2} sec^{-1} normal to the sun's rays, causing a production of 2×10^{8} ion pairs cm^{-2} sec^{-1}, being necessary to account for the more prominent wireless facts. In the present case we have brought into view effects due to 4.1×10^{-5} erg cm^{-2} sec^{-1} ultra-violet radiation flux, which for the most part is so highly absorbed that the ionization which it produces is above a 200 km level. The point to be emphasized is that the present notions supplement, without disturbing, the Kennelly-Heaviside layer theory. In one instance they contribute an explanation of a fact about which the older theory was none too clear. The fact, which was discovered while the older theory was being developed, is that wireless signals of short wave-length, 16 meters or so, traverse polar regions without being lost. This is shown by certain round-the-world signals, and by the excellent direct communication being maintained with short waves between this Laboratory and the Byrd expedition in the Antarctic areas. On the earlier theory it was difficult to understand how there could be sufficient ionization to permit this, merely because the sunlight is so weak in the polar regions. It is seen now, however, that a large part of the polar ionization may be due to the influx of high flying ions from the lower sunlit latitudes which may amount to (see section 7) $10^{6}\times1.3\times10^{13}\div4.34\times10^{16}=3\times10^{7}$ ion pairs cm^{-2} sec^{-1} or more in the polar regions.

9. *The ion pairs at 42,200 km, and the sweeping up by the earth of the ions of space.* It was shown in section 7 that due to centrifugal force the ion pairs formed above 42,200 km in the plane of the magnetic equator will rarely return to the earth. The ions will remain at this level and therefore, when they accumulate sufficiently, will form a sort of a ring around the earth. The ion density in the ring will depend upon the rates of loss and supply of the ions. After a sufficient density has been built up in the ring some of the ions may receive velocities, due to collisions, of the proper magnitude and direction to drive them down along the magnetic lines of force to the polar zones of the earth. The density of the ring and this loss is probably not very great during solar quiescence. The rate of loss may be estimated from the frequency of collisions, but the rate of supply is pretty uncertain. There are two sources from which the ions may come, (a) the terrestrial atmosphere and (b) the ions of space which are swept up by the earth as it moves through space. The number of ions from the first source can be estimated from the number of high speed atoms, that from the second may be gotten from

Eddington's[16] estimates of the ion density of interstellar space; it seems that the two effects may be of the same order of magnitude. However, we will not go further with the problem now; a complete solution would involve the description of what happens when a rotating magnetized conducting sphere moves through a pure ion gas. The possible bearing which all of these ideas may have on the escape of planetary atmospheres, solar corona, zodiacal light, rings of Saturn, etc., is left to the future.

It must be pointed out that in the foregoing discussion of the ion ring and in various places throughout this paper we make use of the idea that the ion pairs are caught on the lines of force of the earth's magnetic field as if these lines of induction were material filaments attached to and rotating with the earth. It is clearly realized that such a conception can hardly be entirely correct, but to what extent it is incorrect we are uncertain. Future modifications of the present theory will be involved in the solution of the problem. Theories of unipolar induction (*Vide*, Nat. Res. Coun. Bul., vol. 4, No. 27, 1922) indicate that ion paths near a rotating magnet may be calculated as though the lines of induction rotated with the magnet, and at a distance as though the lines lagged behind the magnet. Such theories require assumptions as to the nature of the magnet and we are not sure to what extent they are capable of describing the effects at a distance from the earth. The reactions of the ions on the field may be important.

10. *Solar activity.* It is assumed that the sun when active sends out a blast of ultra-violet light for half an hour, or 1.8×10^3 sec. For example, if 1/10,000 part of the solar surface, which normally is at a temperature of 6000°K, were removed and there were exposed the blackbody radiations from regions at a temperature of 30,000°K, the total solar radiation in wave-lengths from 0 to ∞ would be increased by 6.3 percent. The solar energy in wave-lengths from 3000A to ∞ would be increased by 0.74 percent, and at wave-lengths 3500, 4000, 5000 and 6000A by 3.2, 1.7, 0.75 and 0.32 percent, respectively. Corresponding values which are observed[17] in the short interval (an hour or so) variations of the solar energy are roughly 1, 8, 2, 1 and 0.2%, and often times more. On the whole the observations indicate a higher temperature of the solar volcanoes than 30,000°K. The hot spot, or spots, will be brighter than the surrounding 6,000° surface by factors of 734, 320, 168, 75 and 32 at wave-lengths 3000, 3500, 4000, 5000 and 6000A, respectively. Whether such bright spots can be, or are observed we do not know—we must leave the question to the astronomer; bright spots, often near the sun spots, and regions bright in particular wave-lengths are of course observed on the sun. Calculations of brightness based on assumptions of black body conditions are at best only approximations, and perhaps very distant ones, in such a case where line emission and absorption undoubtedly play a predominating rôle. When we speak of the flash lasting a "half hour," all that is meant is that the flash remains at full intensity for some minutes

[16] Eddington, reference 11, page 382; Struve, Astrophys. J. **67**, 353 (1928).

[17] Annals of the Astrophys. Observatory of the Smithsonian Institution IV, pages 17 and 207; Smithsonian Miscellaneous collections, **80**, 10 (1927).

or hours and then dies away in a day or so; it might of course flare out again intermittently or irregularly.

In Table II are given the values of the solar energy in erg cm^{-2} sec^{-1} received outside the atmosphere of the earth in various wave-length regions for a quiet sun S_q and an active sun S_a, i.e. the sun with the hot spot, or volcano, of the preceding paragraph, and the ratios S_a/S_q, assuming black-body conditions for the calculations. The table shows that the solar energy in the far ultra-violet is greatly increased when the sun becomes active and that the energy in the longer wave-lengths is little changed.

TABLE II. *Solar energies received outside the earth's atmosphere.*

Wave-length region	Quiet sun S_q	Active sun S_a	S_a/S_q
0 to 800A	4.6×10^{-4}	7.3×10^{2}	1.5×10^{6}
800 to 1000	0.1	8.0×10^{3}	8×10^{4}
1000 to 1500	87	1.3×10^{4}	1.5×10^{2}
1500 to 2000	4.9×10^{3}	2.9×10^{4}	6.0
2000 to 2500	1.6×10^{4}	2.5×10^{4}	1.54
2500 to 3000	2.0×10^{5}	2.3×10^{5}	1.15

11. *Some general effects of the Solar ultra-violet flash on the temperature, winds, ionization, ozone, aurora light, etc., of the high atmosphere, and on comets.* In later sections it is shown in detail how the solar ultra-violet flash gives rise to magnetic storms, but before doing this it is of interest to examine in a descriptive manner the effects of the flash on other phenomena. The actions of the flash will occur mainly in the high atmosphere, for it is largely the wave-length region below λ3000, a region absorbed in the high atmosphere, which varies with the flash. From Table II it is seen that the energy from λ1500 to 3000 is increased roughly 10 times by the solar bright spot. Assuming, as in section 2, that this energy goes into heat the atmospheric temperatures and pressures were calculated just as for the quiet sun, and are given in columns 6 and 7, Table I. The calculation assumed thermal equilibrium above 150 km; an acceptable assumption for it was seen that equilibrium would be reached within a few minutes. The diffusion level was at about 450 km and the level above which there were practically no collisions was at 800 km. Table I shows that the energy blast heated and expanded the atmosphere above 50 km causing it to move upward 100 km or so. Thus the maximum of ionization[2] which for the quiet sun is at 190 km would be moved up to 290 km. Hafstad and Tuve[18] observed an increase in the apparent daytime height reached by 70 meter wireless wave pulses from this Laboratory of about 100 km during the strong magnetic storms of October 7 and 18, 1928. In addition to heat, the ultra-violet blast causes an increase in the high atmospheric ionization which may be felt as low as 100 km where the atmospheric absorption of short wireless waves (less than 100m) occurs. The absorption of these waves is therefore augmented

[18] Hafstad and Tuve, Terr. Mag. and Atmos. Elec. **34**, March (1929).

during solar activity, and it is well known that wireless communication, especially with short waves, is interrupted during magnetic storms. The present theory indicates that the disturbance of wireless should occur a short time after the commencement of the magnetic storm, and a comparison of the wireless log books of this Laboratory with the records of magnetic storms showed that this was less than two hours. Further, the short wave wireless data, for waves below 50 meters, showed that *when the magnetic storm began it was the wireless communication on the daylight side of the earth which was interrupted, and that communication on the night side was not disturbed at all.* The night communication channels were interrupted at dawn, as the rotation of the earth brought them into the sunlight. This is regarded as direct evidence in support of the solar ultra-violet light hypothesis of the present theory and in contradiction to the hypotheses of charged particles ejected from the sun advanced by others [21,25,28] to account for the magnetic storms. For the solar charged particles were supposed to strike the night as well as the daylight side of the earth, and therefore would be expected to disturb wireless on all sides of the earth. The complete investigation will be given in another paper.

One would expect the ultra-violet blast to make an appreciable change in the ozone of the high atmosphere, but there seems to be no clear connection between ozone variations and solar activity.[19] The energy of the light in the ozone-forming spectrum region λ1500 to 2000 or 2300 is increased to be sure, but other factors such as pressure, water vapor, etc., may be as important as light intensity in the production of ozone. The increased pressure gradient from day to night areas in the 50 to 150 km levels (see columns 3 and 7 Table I) will cause strong winds in the high atmosphere which may scatter about any unusual formations of ozone. The potential energy of ionization and excitation in the high atmosphere is increased by the ultra-violet light flash and therefore the light of the night sky, or the non polar aurora, which owes its origin to a portion of this energy,[2] would be expected to increase in intensity during periods of magnetic disturbance. Rayleigh's[20] preliminary measurements indicate this; he observed an average increase in the night sky luminosity during four years of increasing sunspots. Babcock[7] observed an unusual brightness in the non polar aurora during the nights of July 11-12 and 12-13, 1922. There was a strong magnetic storm (strength 2) from June 27 to July 4, an unusual length, and a moderate one (strength 1) from July 13 to 20, 1922.

The number of ions and excited atoms above 200 km will be enormously increased by the solar flash, by a factor of 10^5 perhaps, because the energy in the ionizing region below λ1000A is increased by this much during solar activity (see Table II). The number of high speed atoms will be greatly increased, but because of the greater intensity of the ionizing light these will be ionized very soon (see equation (1)), before they have had time to reach great heights. Being unable to shake off the entangling influence of

[19] Dobson, Proc. Roy Soc. **114**, 521 (1927); Buisson, Comptes Rendues **186**, 1229 (1928).
[20] Rayleigh, Proc. Roy. Soc. **119**, 11 (1928).

the earth's magnetic field the ions will be held in levels below, say, 2000 km. Therefore, the ionic distillation to polar latitudes, and hence the aurora intensity, will not increase by any such factor as 10^5, it may even decrease during the ultra-violet flash. After the half-hour flash begins to die down, the unusual flood of energy left in the high atmosphere in the form of heat ionization and excitation gives rise to an unusual number of high flying ions which stream to the polar regions and cause an unusual aurora display. At the same time there will be strong winds in levels 400 to 1000 km blowing mainly to the north and south, the east and west currents being relatively less because of the guiding effects of the magnetic field upon the ions. This results in an unusual tumbling in of ion pairs into the atmosphere of middle latitudes, and hence in auroras in these latitudes. This gives an explanation of the aurora displays at latitudes as low as 40° often seen in times of intense solar disturbance, the irregular flickering and shifting clouds and patterns of luminosity being exactly the type of display that one would expect to arise from windstorms in the high atmosphere.

The ultra-violet blast would be expected to cause changes in comets, much as it does in our own atmosphere, and we find that this actually happens. The complete investigation will appear in another paper. For, in nearly every instance the date on which a comet was observed to undergo an unusual change, such as breaking up of the nucleus, loss of tail, sudden increase in brightness, etc., was found to follow within a few days the date on which a strong magnetic storm occurred on the earth, provided the necessary condition was fulfilled that the earth and the comet were approximately on the same side of the sun. When the comet and the earth were on opposite sides of the sun, changes in the comet were found to occur between periods of terrestrial magnetic storms separated by one half a solar revolution. One might possibly expect changes in the appearance of Jupiter, Venus and the rings of Saturn to be connected with terrestrial magnetic storms.

12. *Data of magnetic storms.* The important facts of magnetic storms have been summarized by Chapman[21] in his extended analysis of the observations of many observatories of many storms. Certain data of interest in the present discussion are given in Figs. 3 and 4. The magnetic field variation is given by the variation in the horizontal field HF, the vertical field VF and the western declination WD, the angle through which the compass deviates to the west from its position on magnetically quiet days. The total magnetic variation at any station is made up of three parts, (1) a quiet day variation characteristic of the latitude of the station, etc., (2) a world wide storm variation and (3) a diurnal storm variation. The theory of the quiet day variation has been worked out by Gunn,[3] that of the storm is given in the following pages. The curves of Fig. 3 give the main facts of the average world wide storm for the temperate zone; the world wide storm occurs simultaneously (within a minute) over the whole earth; the abscissas of the curves are in hours from the beginning of the storm. The HF increases

[21] Chapman, Proc. Roy Soc. **A95**, 61 (1919); **A115**, 242 (1927).

rapidly to 50y, or 100y for a strong storm, ($y = 10^{-5}$ gauss) in a half hour or so, decreases to negative values in several hours and finally ascends to zero in several days. The VF is at first negative then positive, the variations being on the whole small, less than 10y. The WD variation is small and irregular. The curves of Fig. 3 show that the HF values are slightly less, and the VF and WD values slightly greater, at the higher latitudes. The curves of the diurnal storm variations at various magnetic latitudes are given in Fig. 4, the abscissas being local solar time. These diurnal variations persist with lessening intensity for a day or more. The curves for latitudes 22, 51, 58 and 61 are taken directly from Chapman's paper, the curves for latitudes 70° are sketches which give the characteristic type of the variation within the aurora zone omitting many complexities and irregularities which are often observed in this region.

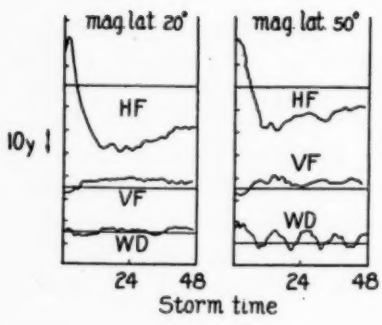

Fig. 3. World-wide storm variations of the components of the earth's magnetic field at various latitudes plotted against hours from the beginning of the storm.

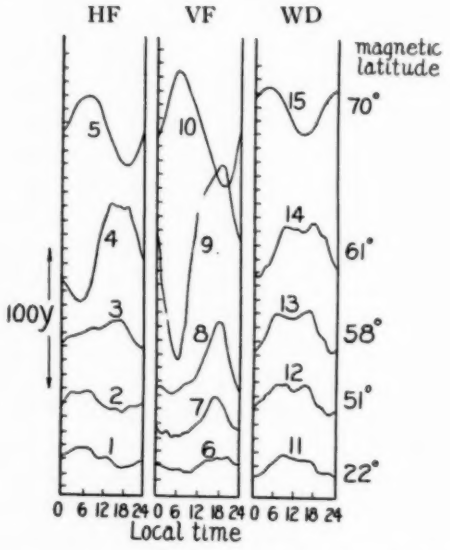

Fig. 4. Diurnal storm variations of the components of the earth's magnetic field at various altitudes plotted against local solar time.

13. *The theory of the world-wide magnetic storm.* From columns 5 and 6, Table I, it is seen that the heating effect of the solar ultra-violet flash expands the terrestrial atmosphere causing particles in the outer levels above 400 km to move upward 500 km or more, and, as shown in section 12, the ionizing effect of the flash is to produce large numbers of ions at fairly low levels between 1000 and 2000 km, say. In these regions where the molecular densities are 10^9 or less, and the temperatures are around 1500°K, the free paths are 10^6 cm, or more, and the radii of magnetic gyration 10^4 cm or less. It is the ions produced in these regions which give rise to the world-wide magnetic storm. If the energy of the flash which causes ionization is 10^3 erg cm^{-2} sec^{-1} (see Table II) and the ionization potentials of the atmospheric

atoms and molecules are around 20 volts (3.2×10^{-11} erg), there are 3×10^{13} ion pairs formed per second, or 10^{17} ion pairs in a half hour (1.8×10^{3} sec), in a 1 cm^2 column of the atmosphere. Some of these of course will disappear, by moving to lower levels, etc., so we take it that the number of long free path ions reaches a maximum value of 10^{16}, and then decreases when the flash begins to die down. These ions, no matter what their velocities are, under the combined action of the earth's gravitational and magnetic fields move at right angles to these two vectors with a velocity V, where approximately

$$V=mg/He, \tag{6}$$

the positive ions and negative electrons going in opposite directions. J. J. Thomson[22] worked out the case of an ion moving in crossed electric and magnetic fields, and it is only necessary to replace the electric force Xe in his first equation, page 87, by mg to get our equation (6). The approximation in (6) is due to the assumption, valid in the present instance, that the motion of the ion continue long enough so that periodic terms may be neglected; this in effect neglects (correctly) the kinks in the cycloidal path of the ion. At 1000 km above sea level $H=0.3$ gauss and $g=720$ cm sec^{-2}. With these values in (6) V is 3.9, 3.4 and 1 cm sec^{-1} for an oxygen, nitrogen and helium atom, respectively.

We note that V in (6) is independent of the random temperature velocities and is therefore a drift velocity parallel to the surface of the earth superimposed on the other velocities. Since the positive and negative electrons drift in opposite directions they form an electric current (or, rather, a pulse of current which dies down after the flash of light is over) flowing around the earth from west to east, the lines of current flow being roughly circles in planes perpendicular to the magnetic axis of the earth with centers on the axis. We may picture the positive ions as held in sort of a lattice by their own repulsive forces all moving around the earth, the positive lattice being congruent with a negative electron lattice (probably mostly negative ions on the dark side of the earth) which moves in the opposite direction, the two lattices being pushed by the gravitational magnetic forces which are operative mainly in the daylight regions. Each cm^3 of the atmosphere therefore remains approximately electrically neutral at all times.

The drift current around the earth is strong at the equator and weaker toward the poles, for at high latitudes, above the 40'th parallel (see Fig. 1) at a 1000 km level the magnetic force approaches verticalness and the ions slide down the magnetic line to low levels so quickly that they contribute but little to the drift current. Thus the drift current is in an equatorial belt roughly 5,000 km $=5\times10^8$ cm wide, 10^{16} ions thick, and is at a distance 1000 to 2000 km from the earth's surface. With $V=1$, the current is $5\times10^8\times10^{16}\times1\times1.59\times10^{-20}=10^5$ c.g.s.e.m.u. or 10^6 amp. The current on the dark side of the earth is carried by the normal night-time ionization which is mainly in the levels below 300 km (the Kennelly-Heaviside layer), the total

[22] Thomson, "Conduction of Electricity through Gases," page 87 (1903).

number N of ion pairs in a 1 cm^2 column of the night atmosphere[2] being, say, 10^{15}. From Ohm's law the current i is related to the voltage E by $i = \sigma E$, σ being the conductivity. For an ionized gas $\sigma = Nef/2mu$, where f is the free path of the ions and u their velocity of temperature agitation. The formula neglects the effect of the earth's magnetic field, which is permissible for the night Kennelly-Heaviside layer where the molecular density is 10^{12} or more. With $N = 10^{15}$, $f = 10^2$ cm, $u = 10^3$ cm sec^{-1} and $i = 10^6$ amp, $\sigma = 10^{16}$ c.g.s. e.m.u. and E $= 10^{-9}$ volts. This shows that the night time conductivity of the ionized atmosphere is very high and is easily capable of carrying a 10^6 ampere current. To repeat, it is the mechanical gravitational drag of the long free path ions across the earth's magnetic field which gives rise to the effective voltage 10^{-9} volts.

The equatorial current pulse produces a magnetic field at the surface of the earth of 10^{-2} gauss, or $10^3\gamma$ (a long calculation, see Maxwell[23] for the method), which is in the direction from south to north and therefore increases the horizontal field HF, as is observed. The magnitude of the observed values is $10^2\gamma$ rather than $10^3\gamma$, for the first increase of the storm field (see Fig. 3). Due to the atmospheric current pulse, there is an opposing current induced in the earth, which prevents the storm field from reaching the value $10^3\gamma$. When the atmospheric pulse dies away, which may require several hours, the earth current finally reverses the storm field to negative values, which decrease to zero as the earth current in turn dies away. Thus the theory gives entire agreement with observation. The exact calculation of the induced effects leads far into eddy current theory; rough calculation indicates a reasonable earth resistance and damping constant. Into the calculation enters the time for the atmospheric current pulse to die away, a time which is made of two parts, (a) the time for an ion at 1500 km to crawl down a magnetic line to a 400 km level which is 6 to 14 hours, plus (b) the time for the ultraviolet flash to die away; only a study of the records can decide which of these times predominates in any particular case. Further, it is easily seen that the HF decreases at the higher latitudes and that the VF is small (theoretically zero) at the equator and increases with the latitude, as is observed. The simple theory described here indicates a zero value of WD for all latitudes, and at moderate latitudes WD is observed to be small, but at high latitudes WD fluctuates appreciably with a period around 12 hours. To explain this would require perhaps the careful consideration of many factors which have been neglected, such as the tilt of the magnetic axis, the induced earth currents, etc.

14. *The energy of the world-wide magnetic storm.* The energy of the world-wide storm is derived from the fall of the long free path ions from a storm level of about 1300 km to a quiet day level of 300 km, a fall of 10^8 cm. Each ion loses energy $mgh = 2.3 \times 10^{-23} \times 900 \times 10^8 = 2 \times 10^{-12}$ ergs, for a nitrogen atomic ion. The total number of ion pairs in the daylight section of the current belt 5000 km wide and $\pi \times 6400 = 20{,}000$ km long, with 10^{16} ions

[23] Maxwell, "Electricity and Magnetism," 2, 307 (1873).

above each cm², is 10^{34}. Therefore the total energy of fall is $2\times10^{-12}\times10^{34}=2\times10^{22}$ erg. The observed value, or rather the value which Chapman[24] calculated from magnetic observations in a general manner, on the assumption that the storm was due to atmospheric currents, was 8.3×10^{22} erg. The agreement was of course to be expected, because the equatorial ion current produced the observed storm field 10^2y, and merely serves to bring out details of the present theory. Actually it was realized long ago that an equatorial atmospheric current would cause the world-wide storm, but no satisfactory origin of such a current or the details of the energy exchanges was proposed.

15. *The theory of the diurnal magnetic storm variations.* The first effect of the solar ultra-violet flash is to suppress the ion migration to polar regions, for although many fast moving atoms are produced, they are ionized so quickly that most of the ionization is confined to levels below 2000 km. As the flash dies down the polar ion migration becomes strong and then grows weaker with the dimming flash. Although the exact details are uncertain we may regard the dying away of the flash as the cooling of the 30,000° hot spot. The maximum energy shifts from λ911A to longer waves as the temperature falls. Therefore the energy in the ionizing spectrum region below λ1000 decreases more rapidly than the energy in the excitation region λ1000 to 2000, roughly. As the flash dies away the high flying ions are maintained in considerable number and the time of ionization is such as to bring them into polar regions. Therefore on the daylight side of the earth during a magnetic storm there is an unusual migration of ion pairs to the polar magnetic latitude 67°, a migration which increases during the morning, local time, reaching a maximum at noon, and which decreases again in the afternoon. Since 9 hours (see section 6) are required for the high flying ions to go from the equator to the polar zones, the flux of ion pairs arriving at any specified longitude on the 67° parallel is a maximum at about 21 hours, local time. The ion flux and hence the ion density, therefore increases all day, reaching a maximum at about 21 hours (9 P.M.), and decreases all night. In other words, the cloud of maximum ionization moves around the earth on the 67'th parallel remaining always roughly 9 hours behind the sun.

The ion cloud, which is at a level where the free paths of the ions are long compared to their radii of magnetic gyration, is a diamagnetic cloud, as shown by Gunn.[3] We may calculate its magnetic effects approximately by replacing it by a bar magnet *NS*, Fig. 5. The figure gives a cross section of the northern magnetic quadrant of the earth, the lines of the earth's permanent magnetic field being shown by the curves *a*. The ion cloud magnet lies along a curve *a* at magnetic latitude 67°, with its south magnetic pole fairly well concentrated and about 200 km above the earth's surface, and with its north magnetism spread out into the upper atmospheric regions. The field of this magnet is shown in curves *b*, Fig. 5; to this field should be added the field of the similar ion cloud in the southern polar zone, which is, however, practically negligible in the northern latitudes above the tropics.

[24] Chapman, Roy. Ast. Soc., Monthly Notices, **79**, 70 (1918).

The curves *b* yield at once diurnal storm variations in general agreement with observation. The increase or decrease, in the *HF* and *VF* values to a maximum or minimum at 7 to 10 P.M. is due to the fact that the magnet *NS*, Fig. 5, is nearest to the station at this time. The curves *b* indicate that at low latitudes *HF* should increase during the day and decrease at night; the observed curves 1 and 2, Fig. 4 show just the reverse of this, and we are not sure to which of the many simplications and omissions of the theory the discrepancy is to be attributed. At the higher latitudes, however, the theory is in exact agreement with observation, for curves *b*, Fig. 5, show that in latitudes below the auroral zone 65° the value of *HF* increases all day, in accord with curves 3 and 4, Fig. 4, and above the auroral zone it decreases all day, as in curve 5. It follows from curves *b*, Fig. 5, that the

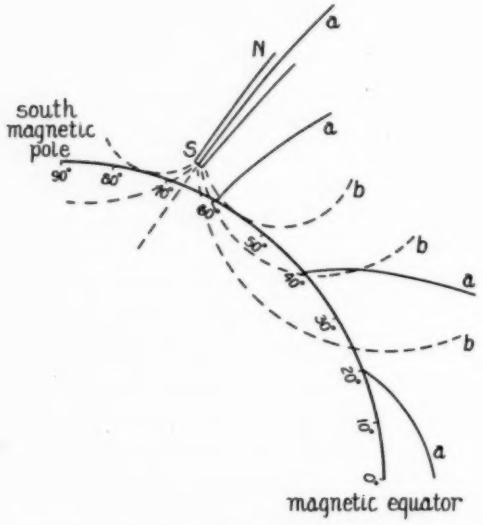

Fig. 5. Curves *a* are the permenant magnetic field lines of the earth's field. Curves *b* are the additional magnetic field lines due to the ionic cloud in the auroral zone during a magnetic storm. The cloud is roughly equivalent to the bar magnetic *NS*.

VF variation increases with the latitude, passes through a reversal at about 55°, and reaches high values in auroral latitudes, in exact accord with the observed curves 6 to 10, Fig. 4. Without giving obvious details it is seen that the *WD* at any station falls off during the day to a minimum in the early evening and then increases during the night. This agrees fairly well with the observations of curves 11 to 15, Fig. 4, with the exception of the afternoon humps of curves 12, 13 and 14. If the angle between the magnetic and geographic axes is taken into consideration, the theoretical *WD* curves get humps which vary with the longitude of the station. This is readily worked out with a pasteboard globe, plenty of pins and a strong geometrical imagination. We are uncertain whether the humps are to be attributed entirely to this, or perhaps also to some of the other simplifications introduced into the theory, or to the effect of induced earth currents.

Thus far the diurnal storm variations have been considered only qualitatively. To make quantative estimates we recall that in the Kennelly-Heaviside layer on a quiet day the maximum ion density may be as much as 10^9 or 10^{10} (reference 2, page 1033). Due to the unusual poleward ion migration during a magnetic storm we may expect a maximum ion density n as high as 10^{11} or 10^{12} at the 67° zone. For a magnetized long free path ion gas the intensity of magnetization I is given by $I=-3nkT/2H$, (reference 3, equation (16)), where T is the absolute temperature and k is the molecular gas constant 1.372×10^{-16} erg per degree Kelvin. With $n=10^{11}$, $T=1000°$K, $H=0.5$ gauss, $I=4.1\times10^{-2}$. From Poisson's equation the magnetic pole strength per unit area σ is $I/4\pi=3.3\times10^{-3}$. Taking the end S of the magnet NS, Fig. 5, to be 300 km thick and 1000 km wide, the magnetic strength of S is $3.3\times10^{-3}\times3\times10^{15}=10^{13}$. At a distance 3000 km, neglecting the effect of the north pole N, Fig. 5, the field due to S is approximately 10^{-4} gauss or $10y$; or if we put $n=10^{12}$ the field is $100y$. These are the orders of magnitude which are observed, and the conclusion is that quantitatively the present theory is acceptable.

16. *Earlier theories of auroras and magnetic storms.* The well-known theory of Birkeland, Störmer and Vegard[25] attributed the aurora to streams of charged particles emitted by the sun which under the influence of the magnetic field of the earth were diverted to polar regions. The theory has contained a number of difficulties, for example, if the charged particles are α-particles or ions of some sort they do not combine a sufficient penetrating power with a sufficient magnetic deflectibility to explain the height and structure of the aurora,[26] and if they are electrons their penetrating power may be too great.[27] No one, however, has been interested in stressing these difficulties as long as there was no other theory available. An explanation of magnetic storms by means of hypotheses of solar corpuscles, developed by Chapman[21] and modified by Lindemann,[28] was found inadequate to explain the diurnal effects.[21] It is too much to hope perhaps that the ultra-violet light theory as we have given it can stand without future modification. It is quite certain that charged coronal matter may reach the earth and may be active in causing auroral and magnetic effects. It seems, however, that in any outburst from the sun the energy emitted in the form of matter will be much less than that in the form of radiation, and therefore that terrestrial effects due to the radiation are greater than those due to the material stream. Furthermore, the ultra-violet radiation theory has been found adequate to explain the observed complicated distribtion of the phenomena over the surface of the earth without the many *ad hoc* hypotheses which would be necessary to a corpuscular theory.

NAVAL RESEARCH LABORATORY,
WASHINGTON, D. C.
November 27, 1928.

[25] Müller-Pouillets, Lehrbuch der Physik, **5**, 484 (1928).
[26] Vegard, Phil. Mag. **46**, 211 (1923).
[27] Swann, Phil. Mag. **47**, 306 (1924).
[28] Lindemann, Phil. Mag. **38**, 669 (1919).

SOME POLARIZATION PHENOMENA OF VERY SHORT RADIO WAVES

By Eugene A. Paulin

Abstract

Survey of the intensity and state of polarization of the radiation field in the vicinity of a short-wave oscillation generator.—A new type of detector, patterned after the design of S. L. Brown, was found to furnish an excellent means for conducting this survey. The intensity and state of polarization of the radiation field at distances up to 100 meters from the oscillator were examined. The wave-length range was from 5 to 7.5 meters. It was found that the loop of the oscillator and the linear radiator coupled to it imprint their character on the polarization of the waves. The wave is the result of components which have their source in the individual current-carrying elements in the radiating system. It was also found that the state of polarization of the waves, at least within the range of distances covered by this survey, shows no tendency to change as the waves proceed out from the generator. This is at variance with the statement of Pickard who finds the reception is predominantly horizontal. Interference effects were observed which indicate the importance of secondary radiations which may come from conductors in the immediate vicinity of the sending and receiving sets. They were found to affect materially the intensity and the state of polarization of the total radiation received.

Beam sending.—It was found that by simple means, a beam of short waves could be sent in any direction. By the addition of tuned rods the beam could be made increasingly concentrated.

I. Description of Apparatus

The Transmitter

THE transmitter used throughout this investigation, is substantially the same as described by J. Tykocinski-Tykociner in his "Investigation of Antennae by Means of Models."[1]

Fig. 1 shows the principle of this high-frequency oscillator. A loop is divided symmetrically into two parts, one above and one below the bakelite panel. The two parts of the loop are connected by means of two condensers. One of the condensers, C_0, is variable, having a capacity range of from 3 to 15 $\mu\mu f$. It consists of two semi-circular plates about 5 cm in diameter, separated by a variable air-space. The other condenser C_v, is formed by the plate and the grid of the vacuum tube V, which is a Radiotron, Model UX-852, having a capacity of about $10\mu\mu f$. This tube was designed by the Radio Corporation of America for use as an oscillator or power amplifier, particularly adapted to wave-lengths under 100 meters. In order to facilitate its use under these conditions, the interelectrode capacities have been made low and the insulation between electrodes high, by mounting each electrode on a separate support. The normal voltage for the filament is 10 and for the plate 2000, although in the following experiments only 720 volts were

[1] Tykociner, Univ. of Ill. Bulletin **147**, Eng. Exp. Station (1925).

used. Choke coils a, b, and d are inserted in the leads connecting the plate circuit and the filament circuit with their batteries, for the purpose of suppressing oscillations in these leads.

A comparatively large condenser C_2 (0.002 μf) is inserted in the middle position of the loop to prevent a direct connection of the plate with the filament should C_0 break down. The by-pass condenser C_1 (0.5 μf) prevents the flow of high-frequency current through the filament. The thermo-ammeter A_t is inserted in a convenient place to indicate the maximum effective current in the loop. The zero potential leads z_1, z_2, connecting two symmetrical nodal points n_1, n_2, on the loop, contain the grid leak r of about 25,000 ohms on the grid side and a choking coil a on the plate side.

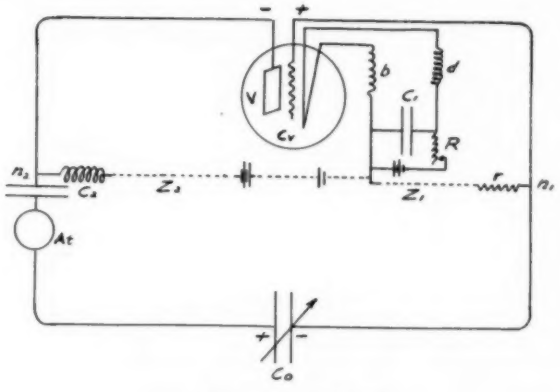

Fig. 1. Transmitter.

By means of an insulated exploring wire, the nodal points n_1, and n_2, can be easily found, and the points where the zero potential leads z_1, and z_2, must be attached are thus determined. The amplitude of oscillation is rapidly decreased by shifting these leads in the direction toward the condenser C_0 or C_v. Proper selection of the points for connecting the leads z_1, and z_2, and proper adjustment of the condenser C_0 are therefore essential to the efficient production of oscillations.

Under these operating conditions, frequencies of from 40 to 60 millions per second are obtained, corresponding to wave-lengths of from 7.5 to 5 meters.

The Detector

The detector[2] used in this series of experiments, furnished an accurate and reliable method for the survey of the field intensity and the polarization conditions in the immediate vicinity of a short-wave oscillator. As actually used, its range was from 5 to 7.5 meters, but by slight adjustments its range can be changed so as to cover somewhat shorter and considerably longer waves. For the longer waves the tuned antenna would become cumbersome and this is the only feature tending to limit its adaptability to longer

[2] The detector is an original design due to Dr. S. L. Brown, and constructed by Mr. Louis Gruber of the Department of Physics, University of Texas.

waves. It is an analyzer in the strict sense of the word, similar to a Nicol prism as used in optics.

Fig. 2 shows the connections of the receiving system. The d.c. meter has a range of 25 micro-amperes and the connections are of the Moullin type. The vacuum tube is a UX-199, and the filament current is furnished by a 4.5 volt dry battery, in series with a constant resistance R_1 and a variable resistance R_2 · R_1 is a coil of manganin wire of 20 ohms resistance which also acts as a choke coil. R_2 is a variable resistance and by means of it the zero and consequently the sensibility of the meter can be regulated. A condenser C_2 is shunted across the filament to prevent oscillations in its circuit. The plate has no separate battery but depends upon the same source as the filament. The grid is maintained at the same potential as the upper part of the step-disk condenser by means of the short loop L.

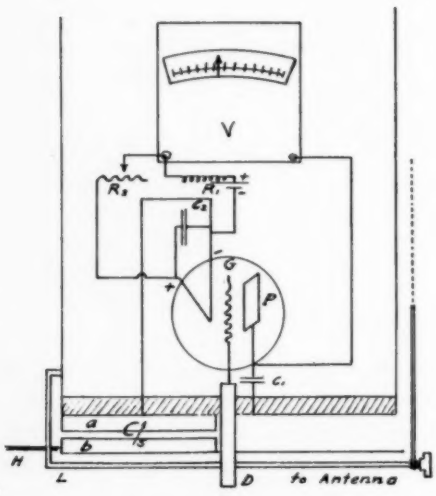

Fig. 2. Detector.

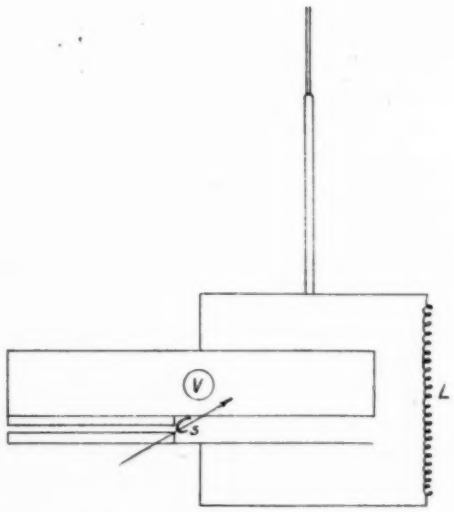

Fig. 3. Diagram of detector system.

The condenser C_s is of special design due to J. Tykocinski-Tykociner and is described in detail in Bulletin 147 of the Engineering Department of the University of Illinois. There are two difficulties encountered in designing detectors for very short waves. The first is the influence of the observers and conductors near the condenser. The step-disk condenser minimizes the effect of surroundings due to the fact that its stray field is small and remains small throughout its range. In the usual type of interleafing condenser the intensity of the stray field varies with the relative position of the plates, and is largest when the position of the plates corresponds to minimum capacity. The second difficulty is due to the necessity of very fine adjustment. A vernier condenser is out of the question in this case, since the stray field would be unduly increased by the addition of an extra plate.

The condenser which was finally evolved from these considerations, consists of a pair of circular aluminum disks. Both inner surfaces of the disks

facing each other are divided into two semi-circular parallel parts, each of them on a somewhat different level. To shield the vacuum-tube voltmeter which was used to detect resonance, its entire circuit was enclosed in a brass cylinder connected to the upper disk, thus forming an integral part of the condenser. The lower member b can be rotated by means of the long wooden handle H and in this manner small variations of capacity can be produced by comparatively large angular displacements of the rotating disk. A sheet of bakelite is placed at the bottom of the cylinder to insulate the instruments from the condenser C_s.

The antenna, which is a rod tuned to the length of the wave being investigated, is fastened at its end to a bar which makes contact with the lower plate of the step-disk condenser. The entire apparatus is pivoted at D, the antenna itself can be rotated in a vertical plane about its point of attachment, so that there is practically a universal joint for the antenna, permitting a survey in any plane. Fig. 3 shows diagrammatically the electrical connections in the detector, the measuring instruments being encased in one plate of the condenser.

Calibration of the Instruments

Calibration of the step-disk condenser. In order to know the wave-length used throughout this series of surveys, it was necessary to calibrate the scale attached to the step-disk condenser. For this purpose the oscillator was set up in the laboratory and by appropriate coupling, a set of stationary waves imposed upon Lecher wires, antinodes of current being located by means of a hot-wire ammeter, and the distances between the antinodes were then measured with a meter stick. At the same time, the detector was tuned into resonance, and the reading of the condenser noted. No attempt was made to measure the capacity in μf, the numbers simply corresponding to the arbitrary scale affixed to the stationary disk of the condenser.

Calibration of the meter in the detector. To obtain the comparative field intensities from the deflections of the meter, the filament current in the oscillator was varied so as to change the current in the loop. Since the radiation from the loop is proportional to the current oscillating in it, the relation between the field intensity and the meter deflection was obtained by setting these loop currents against the deflections of the meter, while the detector was set up at a distance of 35 meters from the sending station.

II. Radio Field Surveys

Preliminary observations indicated that reflections and re-radiations from buildings, wires and passers-by produced such disturbances, that it was decided to move the apparatus to an isolated position about five miles north of Austin. The instruments, including a 720 volt B-battery, were housed in a small cabin, and all disturbing influences, such as trees, screens, and wires removed. The terrain is practically level and afforded an ideal spot for the problem in hand. The plot surrounding the cabin was surveyed, and radii for every 45 degrees marked by pegs placed 10, 20, 30, 40 meters from the

generator. The polar coordinate system was used in designating these points, the initial line going directly east from the oscillator.

In making the survey, the detector was set up at various stations, with the observer on the side toward the oscillator. The antenna rod was revolved in a vertical plane, and readings taken at various azimuthal angles, the horizontal line going to the right of an observer, as he faces the sending station, being taken as zero degrees.

1. *The first survey* was made with the loop of the oscillator horizontal, the sides containing maximum current running north-south. The current oscillating in the loop was 1.5 amperes. At resonance the step-disk condenser showed 3.0 which corresponds to a wave-length of 5.68 meters.

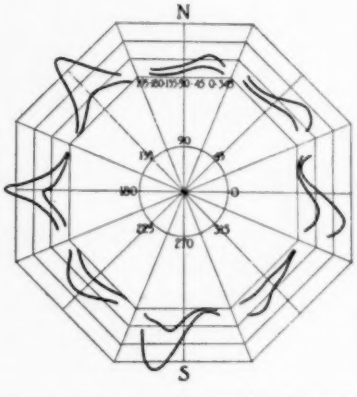

Fig. 4. Graph with loop horizontal.

Fig. 4 shows the distribution of the radiated field, 30 meters and 40 meters from the oscillator. This graph can be pictured as the development of an octagonal prism, circumscribed in the one case at thirty meters and in the other at forty meters from the sending station. Ninety degrees marks the position in which the antenna was vertical, azimuth = 90 degrees, the other typical positions being 45 degrees apart on either side. In each octant, therefore, the abscissas indicate the azimuth, and the ordinates, the deflections of the detector.

A horizontal loop would be expected to radiate a strong horizontal electric field. There are at least three facts militating against a better agreement between the actual results, and what we would be led to expect, namely: 1. induction caused by the earth, 2. vertical fields set up by parts of the apparatus, especially the leads from the B-batteries, and 3. shielding by parts of the oscillator. The earth induction is in consequence of the current in the antenna inducing a flow in the earth, and this in turn, reacting upon the antenna. This causes the maximum field to appear to be above the horizontal. A vertical field, caused by standing waves set up on the leads, is present in all the experiments, so that not a single instance can be given of a pure horizontal field. The high-voltage leads were coiled, crossed over each other, placed inside separate wire sheaths connected with the ground, and later the batteries were raised on boxes in order to shorten these leads, but the vertical field persisted.

2. *The second survey* was made with the plane of the loop vertical and extending in a north-south direction. Fig. 5 shows the distribution at a distance of 40 meters. The fields in the east and west directions are weak, as would be expected. The south octant is exceptionally strong and the northeast is likewise accentuated. This asymmetry is probably due to absorption or re-radiation by parts of the apparatus.

In this case we have a vertical field without admixture, and the diagram shows clearly a vertically polarized wave. Whatever the origin of the subsidiary radiations, they are all vertical, and their vector sum, therefore, must likewise be vertical.

3. *The third survey* was made with the loop horizontal and with a linear tuned radiator pointing north-south along the west end of the loop and in its plane. The vertical fields discussed in the first survey still persist, and as these are not in phase with the currents in the oscillator and radiator, a complicated field results. Elliptical polarization is evident in six of the octants, the west and southwest sections showing plane polarization.

The meter in the loop showed 1.3 amperes, and that in the linear radiator, 0.27 amperes. The survey was made in the 30 meter circle, as shown in Fig. 6. Two readings, in addition to those of the previous surveys, were taken at

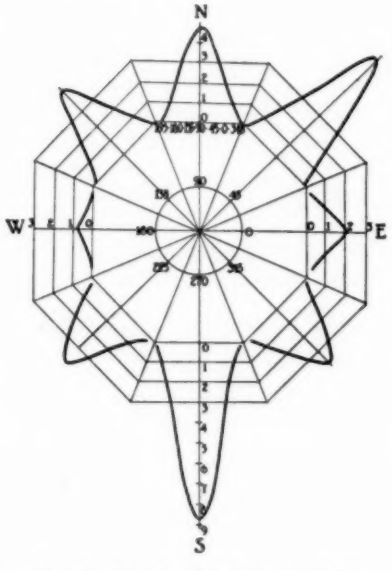

Fig. 5. Graph with loop vertical.

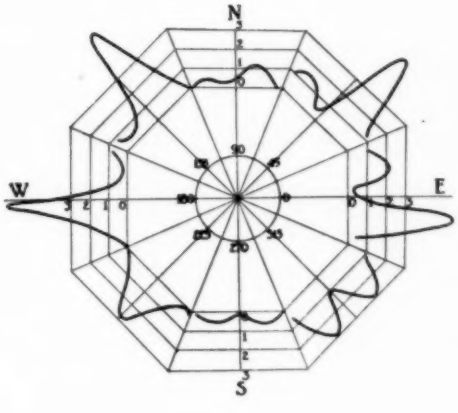

Fig. 6. Graph with loop and radiator horizontal.

each station, one on each side, with the antenna pointing 15 degrees below the horizontal.

4. *The fourth survey* was made with the loop vertical and the linear oscillator suspended in the plane of the loop and pointing north-south. The loop had a current strength of 1.2 amperes and the radiator 0.21 amperes. Fig. 7 shows the field on a 30 and on a 40 meter circle.

Fig. 7 shows the field to be purely vertical in the north and in the south octant, as is to be expected, since the horizontal linear radiator will add nothing in these directions, as it points north-south. The graph likewise shows that, though the intensity of the field weakens as we go away from the sending station, the character of the field remains unaltered.

5. For *the fifth survey*, the oscillator was raised about two meters from the ground, the loop was set vertically in a north-south direction, and the tuned

linear radiator was suspended vertically in the plane of the loop, along its south side, and about 5 cm from it. As the field was very strong, it was necessary to conduct this survey, farther from the oscillator. Distances of 60, 80, and 100 meters were taken as shown in Fig. 8. The loop current was 0.8 amperes, and the radiator current 0.39 amperes.

Fig. 8 shows conditions of perfect vertical polarization, all radiators, principal as well as subsidiary, being in a vertical position. The increased intensity in the southern octant is easily accounted for from the fact that the linear radiator is on the south side of the generator; the decreased intensity in the northern octant is explainable on the same grounds. This survey furnishes a beautiful illustration of the fact, that the plane of polarization does

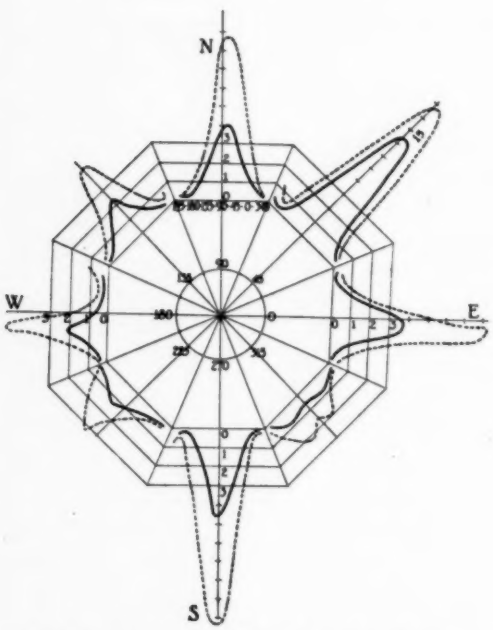

Fig. 7. Graph with loop vertical, radiator horizontal.

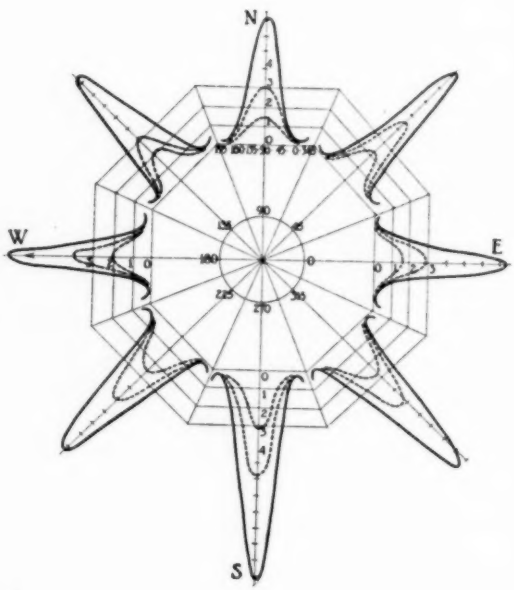

Fig. 8. Graph with loop and radiator vertical.

not tend to tilt, as has been maintained by certain observers, as the waves proceed from the oscillator. At least this was not the case within a range of 100 meters, which corresponds to about 20 wave-lengths.

In all the above surveys, a check was made upon the first reading taken in each circle, so as to be sure that conditions had not changed in the meantime.

Attenuation of the field with distance. As has been pointed out, the character of the field does not change with distance. A quantitative measure of this weakening is furnished by the data in Table I. The measurements were taken with the loop of the oscillator vertical and a linear radiator suspended vertically, the current being kept constant throughout the experiment. The detector, with the antenna fixed vertically, was placed successively at dif-

ferent distances, and the deflections noted, as given in the following table. By means of calibration of the meter in the detector, these deflections were translated into comparative intensities, and the results appended in Table I.

TABLE I. *Distance survey.*

Distance	Deflections of Detector	Corresponding Intensities
40	16.0	1.70
50	9.7	1.38
60	6.1	1.01
80	2.7	.54
100	1.3	.31
120	0.8	.20
140	0.5	.14
160	0.4	.12
180	0.2	.06

By analyzing these results it would appear that the attenuation takes place, approximately, inversely proportional to the square of the distance.

III. INTERFERENCE PHENOMENA

The disturbing influences of surroundings, not only relegated this research to an isolated farm, but also suggested that certain of these disturbances be investigated. In the preliminary observations, it was noticed that the effect of a passer-by was, successively, to strengthen and weaken the field as registered by the detector. The following set of experiments was performed to establish the character of this and similar interference phenomena.

The first of these to be studied, was due to a second observer as he walked at right angles to the line joining sending and receiving stations. The deflections varied according to his position, indicating successive interference and re-enforcement between the wave that came straight from the generator to the receiver, and the wave that was reflected or re-radiated from the observer. Brass rods set up in different positions produced similar effects. A copper screen, carried from the cabin toward the north, while the detector was south of the cabin, caused alternate rising and falling deflections.

By carefully adjusting the position of a copper window screen, placed close to the oscillator, the deflection of the detector was reduced from 9.6 to zero. In the last instance, the silencing of the signal was so absolute, that it was thought that the generator had ceased functioning. The slightest change in the tilt of the screen, however, caused the deflection to re-appear.

A more comprehensive set of observations led to the interference diagram shown in Fig. 9. The data for this diagram were obtained with the loop of the oscillator vertical, and with a vertical linear tube, loosely coupled with it. The detector was placed 40 meters south, and with a clear field, showed a deflection of 10.6. Perpendiculars from the direct line between sender and receiver, were laid off at distances of 2, 5, 10, 20, 30, 35, and 38 meters from the detector, and a second observer walked out along these perpendiculars until a maximum deflection was obtained. These positions of the ob-

server, for which maximum deflections were obtained, were plotted to scale, and the result is the oval of Fig. 9. By taking a series of readings along $C'C''$, $F'F''$, and back of the detector, another series of points was obtained, which resulted in a family of more or less, confocal curves. The distance from the detector to A, the first position for maximum directly back of the

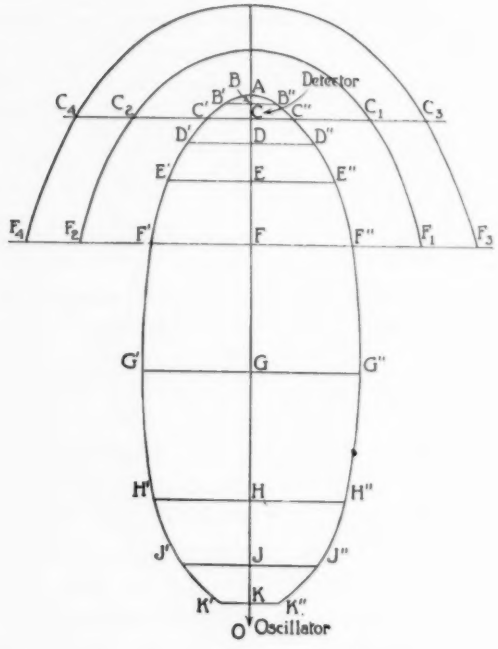

Fig. 9. Interference diagram.

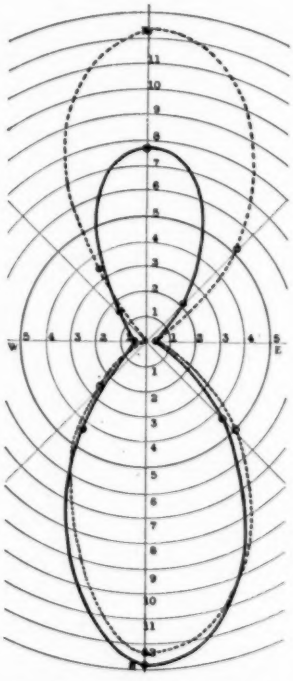

Fig. 10. Beam sending: 4 rods. Solid curve, rods not tuned; broken curve, rods tuned.

detector, was found to be 1.42 meters, which was exactly one fourth of the wave-length used. Other maxima in this direction from the detector were found half wave-lengths apart. The data from which these curves were plotted, are given in Table II.

TABLE II. *Interference data.*

Distances	Deflections		Distances	Deflections	
CA =1.42	12.8		BB′=BB″ =2.25	12.2	12.2
CC′=CC″ =3.5	12.6	12.6	DD′=DD″=4.95	11.8	11.8
EE′=EE″ =6.55	11.4	11.4	FF′=FF″ =7.9	11.6	11.4
GG′=GG″ =8.6	11.0	11.0	HH′=HH″=7.7	11.0	11.0
JJ′=JJ″ =5.4	11.6	11.5	KK′=KK″=2.5	12.4	12.0
$C''C_1=C'C_2=4.9$			$F''F_1=F'F_2=5.55$		
$C_1C_3=C_2C_4=4.6$			$F_1F_2=F_3F_4=4.4$		

Untuned rods were placed at points obtained in the above manner, with cumulative effect, and when eight of them were posted simultaneously,

the resulting deflection was more than double the original, clear-field value. Two Russian investigators, N. Skritzky and W. Lermontoff,[3] noted similar interference phenomena, produced by an observer, walking perpendicular to the line joining the detector to the sending station, but made no attempt at interference diagrams. Neither did they recognize any relation between wave-length and distance between positions producing maxima. They registered the deflections caused by observers of different heights and constitutions, replaced them by rods which gave the same deflection, and speculated upon the use of this method in medical diagnosis.

The explanation of this phenomenon seems to be, that the body or rod, absorbs radiant energy, and re-radiates a part of it by forced oscillations. The interference curves represent the resultant action of two electromagnetic fields upon the receiver, one coming directly from the oscillator, the other from the rod. However, the difference between the direct and indirect paths, do not, as a rule, come out as multiples of half wave-lengths. As noted above, the distance AC came out exactly equal to a fourth wave-length, which is accounted for by the difference in path of half a wave-length between the direct and indirect waves, plus the change in phase of 180°, which would be produced by reflection from the rod. Though the difference in path between the wave coming directly from O to F', thence to C, and the wave coming directly from O to C, is not a wave-length, still the difference between OF_2 plus F_2C and OF' plus $F'C$, is very closely equal to a wave-length. The same can be said of reflection conditions at F_1, F_3 and F_4.

IV. Beam Sending

A final set of experiments was made in directing beams of radio waves. J. K. Clapp and H. A. Chinn,[4] suggested that a directional beam could be obtained by placing tuned linear conductors, fourth wave-lengths apart, on either side of a vertical antenna. The following work indicates the effectiveness of directing beams by comparatively simple methods.

Surveys were made of the resulting field, while the loop of the oscillator was set vertical, and with its plane north-south, as this field was modified by tuned rods. The first set of these surveys was made with four rods placed fourth wave-lengths apart, in the plane of the loop, two on either side. The survey was made on the 30 meter circle, with results as indicated in Fig. 10. For the full curve the rods were not accurately tuned nor accurately placed. Improving these conditions produced the dotted curve.

The second survey was made after the rod farthest to the north was removed, the other three remaining as they were in the first survey. The third survey was made after the second rod to the north was also removed, leaving only the two rods to the south. The full line curve of Fig. 11 indicates the results, when three rods were used, while the dotted curve shows the results when only two rods were used.

[3] Skritzky and Lermontoff, Zeits. d. Hochfrequenztechnik **28,** 82 (1926).
[4] Clapp and Chinn, QST, March (1928).

The last survey was made with three rods, simulating a reflector, placed around the central fourth rod, which was very close to the loop. That is, one rod was placed a quarter wave-length west of the central rod, a second south, and a third east. The distribution of the field is shown in Fig. 12. This diagram shows that a well directed beam is produced by a very simple system of tuned rods.

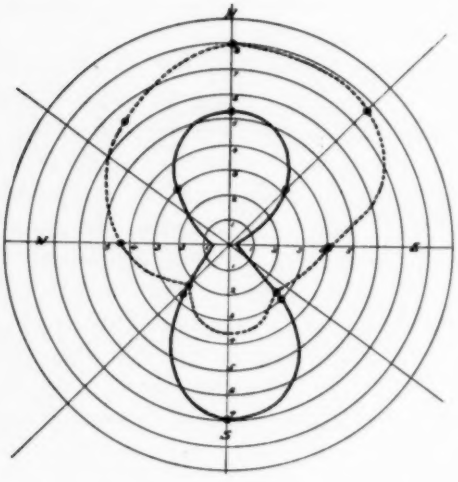

Fig. 11. Beam sending: solid curve, 3 rods; broken curve, 2 rods.

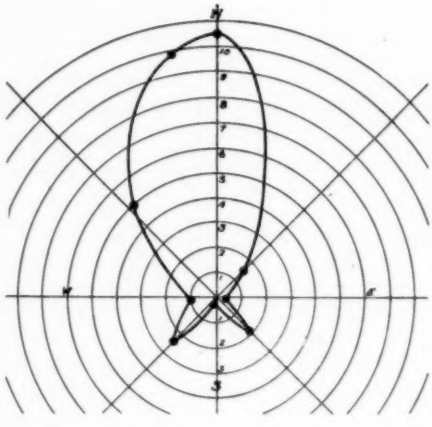

Fig. 12. Beam sending: 2 rods and reflector.

Conclusions

1. The detector herein described, furnishes an excellent means for surveying a radiation field, in the immediate vicinity of an oscillation generator, to establish its condition of polarization. Furthermore, it may be used to measure the distribution of the field from the sending station. This is of particular importance in the case of beam sending, as a local survey, would not only give definite information as to the exact direction of the beam, but also as to its strength. Slight adjustments in the radiating system might produce improvements which would be immediately discernible. This instrument also furnishes a criterion of the success in any attempt at generating polarized radio waves.

As far as known, these surveys are the first to be made by direct galvanometer readings, and demonstrate that reliable, quantitative data are obtainable. This scheme is obviously superior to indirect methods, such as audibility of signals. In this instrument we have a sensitive detector, which may be rotated in a wave front, and the relative strengths of the electric vector indicated by meter deflections.

2. The loop of the oscillator, and the linear radiator coupled to it, imprint their character on the polarization of the waves. That is, the wave is the resultant of components which have their source in the individual current-

carrying elements in the radiating system. Currents which are horizontal, contribute to the horizontal vector, while those which are vertical, contribute to the vertical component. Evidence of this, is the modification of the field concomitant with the rotating of the loop and the directing of the linear oscillator. This seems to contradict the results obtained by Dr. Greenleaf W. Pickard, who says: "Comparative measurements made of radiations, alternately horizontally and vertically polarized at the source, indicated that the ratio of horizontal to vertical electric field, depended only upon frequency, distance, and time of day, being substantially independent of the plane of polarization at the transmitter."[5]

3. The type of polarization of the waves, at least within the range of distance considered in this series of experiments, shows no tendency to change, as these waves proceed from the generator. This statement is particularly borne out by the diagrams in Fig. 8, where the surveys extended as far as 100 meters from the source of the radiations, with the result, that absolutely no change in the plane of polarization was manifest. This is likewise at variance with the statement of Dr. Pickard, who finds that reception is predominantly horizontal. L. W. Austin[6] and R. L. Smith-Rose and R. H. Barfield,[7] found that if the wave was vertically polarized at its origin, it would remain so at all distances, which is in substantial agreement with the findings in this paper.

4. The experiments with interference phenomena, described above, illustrate the importance of secondary radiations, such as may be encountered in dealing with short radio waves. These secondary radiations may come from conductors in the immediate vicinity of the sending and receiving sets, and affect materially the intensity or the polarization of the total radiation received.

5. It has been shown that, by very simple means, a beam of short waves can be sent in any direction desired, and by the addition of tuned rods, can be made increasingly concentrated. This set of experiments was not devised with the intention of developing an improved type of beam transmitter, but to show the applicability of this survey method to the analysis of specialized fields.

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June 16, 1928.

[5] Pickard, Proceedings of Institute of Radio Engineers **14**, 205 (1926).

[6] Austin, Washington Acad. of Science Journal **2**, 101 (1921).

[7] Smith-Rose and Barfield, Proc. Royal Soc. **A107**, 587 (1925); **A110**, 580 (1926); **A116**, 682 (1927).

X-RAY STUDY OF THE SYSTEM PALLADIUM-HYDROGEN

By J. D. Hanawalt

Abstract

A unique *grating parameter* $a_0 = 4.017$A results when palladium is charged with hydrogen either electrolytically or from the gas phase, in disagreement with the results of Linde and Borelius. Larger values of a_0 are possible, but are not stable at 20°C. A difference in stability between some of the electrolytically charged specimens as compared to those charged from the gas phase is associated with the mechanical state of the micro-crystals in the two cases. The concentration Pd_2H is associated with the value $a_0 = 4.017$. *The L_{111} absorption limit* of palladium is changed by the presence of hydrogen which causes a shift of the main edge of 0.87 X.U toward shorter wavelengths, and the occurrence of a secondary absorption 10 X.U. toward shorter wavelengths. This is taken to indicate a chemical combination between palladium and hydrogen atoms. The molecule PdH is suggested. *Impurities* in the palladium affect very markedly its occlusion of hydrogen. The unique value $a_0 = 4.017$ does not appear but rather all distensions in the range 3.885 to 4.030 are observed. It is suggested that impurities in the palladium might account for the difference between the results of Yamada and those of McKeehan.

Introduction

EXPERIMENTAL studies of the system palladium-hydrogen have been made by various methods and by many observers, but there has been some disagreement and contradiction in the results obtained. The method of study in which pressure-concentration equilibria are measured at different temperatures seems to show quite definitely the existence of a hydrogen-rich phase with a concentration very closely in the neighborhood of 0.5 atomic weight of hydrogen per atomic weight of palladium; that is, a composition corresponding to the formula Pd_2H[1,2,3]. The isothermals of Lambert and Gates show 'breaks' at approximately the same composition (about 0.53 atom of hydrogen per atom of palladium) at temperatures of 75°, 103°, and 120°. (See Fig. 1) This phase may be supersaturated to concentrations as high as 0.7. There is, however, considerable difference in the equilibrium pressures obtained by different workers and even question as to whether it is possible to reach truly equilibrium pressures by operating isothermally. Gillespie and Hall consider that equilibrium can be obtained by a special heat treatment. They find 'breaks,' at 0°C at an excess of only 0.2 percent of hydrogen, while at higher temperatures the breaks occur at exactly the Pd_2H composition within the experimental error. In addition to this phase with a hydrogen

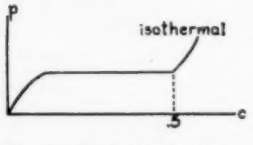

Fig. 1. Relation between hydrogen concentration c in palladium and external hydrogen pressure p at constant temperature.

[1] Troost and Hautefeuille, Ann. Chim. Phys. **2**, 279 (1874).
[2] Lambert and Gates, Proc. Roy. Soc. **A108**, 456 (1925).
[3] Gillespie and Hall, Journ. Amer. Chem. Soc. **48**, 1207 (1926).

concentration of 0.5, there have also been observed states in which the hydrogen concentration is *continuously* increased from zero up to a value greater than 0.5. However, this seems to be just chance behavior, and the causes of it are not understood. The presence of amorphous and crystalline varieties of palladium has been suggested.[4]

Another main line of attack on the problem has been to study the changes in the parameter a_0 of the crystal lattice of palladium when hydrogen is absorbed. Here Yamada[5] finds that hydrogen taken up by palladium from electrolysis of dilute H_2SO_4 may produce a distension of the pure palladium lattice of any amount up to 2.8 percent, and so concludes that the system may best be described as a solid solution of hydrogen in palladium with no indication of a chemical combination. It was found by McKeehan,[6] on the other hand, using either electrolysis of H_2SO_4 or absorption in the hydrogen furnace from the gas phase that palladium and hydrogen are *not* miscible in all proportions, but that two crystalline phases can coexist, one being practically pure palladium with $a_0=3.90$A and the other a saturated solution of hydrogen in palladium with a parameter varying between 4.000 and 4.039, 4.036 being suggested as corresponding to the composition Pd_2H. No suggestion as to the source of the discrepancy between these two investigations has been made as yet.

The latest x-ray study to be published is that of Linde and Borelius,[7] who find quite different results depending upon the method used to occlude the hydrogen in the palladium. By letting the hydrogen furnace form the camera of the x-ray spectrograph, they were able to study the lattice parameter while the specimen was in the hydrogen atmosphere. The results of this experiment showed two coexisting phases, one hydrogen-poor with $a_0=3.89$ to 3.92, and the other hydrogen-rich with an average a_0 of 3.978A which they take to be Pd_2H. By charging the palladium with hydrogen by electrolysis of dilute H_2SO_4 they found a hydrogen-rich phase with a grating spacing larger than that obtained by absorption from the gas phase (4.034 at 20° and 4.023 at 90°). Continued electrolysis was found to produce supersaturation with a corresponding distension up to $a_0=4.07$A. The parameters 4.034 and 4.023 were determined by them to correspond to the hydrogen concentrations 0.70 and 0.65 respectively. Linde and Borelius emphasize the fact that these larger distensions could not be obtained in the hydrogen furnace at the temperatures and pressures at which they worked, nor could the lesser lattice constant 3.978 be obtained by electrolysis no matter how small the current density. Thus the hydrogen-rich phase from the electrolyte is considered by them to be entirely different from that of the hydrogen furnace and the composition $(PdH)_3Pd$ is suggested. This difference is apparently further borne out by the experimental result that the electrolytically charged specimens are more stable than the specimens charged in the hydrogen furnace.

[4] Holt, Edgar and Firth Zeits. f. Phys. Chem. **82**, 513 (1913).
[5] Yamada, Phil. Mag. **45**, 241 (1923).
[6] McKeehan, Phys. Rev. **21**, 334 (1923).
[7] Linde and Borelius, Ann. d. Physik **84**, 747 (1927).

While the work of Linde and Borelius seems fairly complete in itself, yet it is at variance with some earlier results and also with the results to be reported in this paper. The work performed in this laboratory consists of first, an x-ray study of the lattice parameter of palladium as influenced by hydrogen occluded in the palladium (a) by electrolysis; (b) from the gas phase, and (c) by sputtering in an atmosphere of hydrogen; second, a determination of the effect of the occlusion of hydrogen on the L_{III} x-ray absorption limit of palladium; third, a special investigation of the factors influencing the stability of the hydrogen-rich phase; and fourth, a study of the effects on the Pd-H system of impurities in the palladium.

II. Experimental Procedure

For the purpose of measuring the parameter a_0 of the crystal lattice, an x-ray spectrograph of the usual type for working with powdered crystals was used. The tube itself was of the Siegbahn type. A copper anode was used, and the radiation was filtered through a thin nickel screen which also served as the window. The tube was operated at 25 ma and 28,000 volts, and exposures were usually for fifteen minutes. A calcite crystal was used to calibrate the camera, and when taking a diffraction picture, the palladium sheets were pressed against the face of this crystal. The radius of the film-holder was 8.570 cm, and a change in the palladium crystal parameter of about 0.003A could be measured.

The specimens used were from the American Platinum Company; some were 0.5 mm in thickness, while other specimens were rolled into sheets of various thicknesses from 0.05 mm to 0.001 mm. Hydrogen was forced into the palladium from the electrolyte by making it the cathode in dilute H_2SO_4 or HCl or NaOH, platinum being used as the anode. A second method of occluding the hydrogen was to heat the specimens for several hours at 200°C in a fore-pump vacuum, then admit hydrogen to a pressure of one atmosphere, and lower the temperature from 200°C to 80°C in a period of five hours; the temperature is then quickly dropped to 20°C and the specimen taken out and placed in the x-ray spectrograph.

III. Grating Spacing of Electrolytically Charged Pd

Immediately after electrolysis the specimens showed the face-centered cubic lattice with an a_0 varying in the different specimens from 4.017 up to as great as 4.045 (a_0 for pure Pd was determined as 3.885) depending upon the conditions of electrolysis. All specimens with an initial a_0 greater than 4.017 were found to lose hydrogen when kept in air at 20°C until in the course of ten days or less the lattice had shrunk to the value 4.017. In no case was a specimen found to drop below this value, nor did any specimen stop shrinking until it had reached the value 4.017. Specimens with $a_0 =$ 4.017 kept this value unchanged as long as they were under observation (several months). In most specimens this hydrogen-rich phase alone was present, though in some cases the pure Pd, 3.885 or slightly greater, coexisted with this phase. In order to determine whether this particular lattice

spacing 4.017 was simply an equilibrium concentration corresponding to a temperature of 20°C, other specimens were held at temperatures of 50°, 70° and 90°C. As a result of these experiments it was found that the 4.017 lattice would not shrink to smaller values, but that if the temperature was too high, the 4.017 phase would break down completely to the pure palladium lattice. In this process of breaking down, no distension intermediate between 4.017 and 3.885 was observed, the lines of the 3.885 spacing simply appeared and grew stronger and those of the 4.017 phase grew weaker and finally disappeared.

IV. Grating Spacing of Pd Charged from the Gas Phase

The procedure in studying the specimens charged with hydrogen from the gas phase was the same as that described above for the electrolytic specimens. Immediately upon being removed from the hydrogen furnace, the palladium was found to have a face-centered lattice with a_0 equal to 4.017 or very slightly larger (though never reaching the highest values obtained in the electrolyte.) In those cases in which it was larger, it quickly dropped to the value 4.017. In this respect the behavior was exactly like that of electrolytically charged specimens. The behavior was also the same in that no specimens dropped to an a_0 smaller than 4.017. The difference in distension between electrolytically charged Pd and Pd charged from the gas phase as observed by Linde and Borelius did not appear in this work. However, there did appear to be, under certain circumstances a difference in the stabilities of the hydrogen-rich phase at 20°C depending on whether they had been charged electrolytically or from the gas phase. The 4.017 hydrogen-rich phase charged with hydrogen from the furnace was not stable at 20°C, breaking down to the 3.885 of pure Pd in from three to seven days. In this process, no values of a_0 between 4.017 and that of practically pure Pd were observed.

V. Pd Sputtered in Hydrogen

The specimens of palladium which were sputtered in hydrogen were very thin films, probably of the order of 10^{-4}cm thick. Immediately after sputtering the different films showed various distensions of the lattice above 3.885, though none was very large. The lattice constants were all in the range 3.885 and 3.920. By heating a given specimen a few minutes at 300°C in a vacuum, the lattice could be shrunk to a slightly smaller value, and by this means apparently all values of a_0 between 3.920 and 3.885 could be obtained. One specimen produced broad bands instead of lines on the x-ray film, indicating that micro-crystals with a_0's, differing by about 0.01A were existing very close together. After two years in air at 20°C three of these specimens with small distensions showed no observable shrinkage to still smaller values of a_0.

Bredig and Allolio[8] report for palladium sputtered in hydrogen an a_0 of 3.991Å. This large difference may likely be because of a difference in temperature of the cathode in their work and in this.

[8] Bredig and Allolio, Zeits. f. phys. Chem. **126**, 41 (1927).

VI. Influence of the Presence of Hydrogen on the L_{III} Absorption Limit of Pd

In the quest for some property of the Pd-H system which might indicate the nature of the combination, it was decided to determine whether the energy of the L_{III} absorption limit of Pd was influenced in any way by the presence of the hydrogen. A Siegbahn vacuum spectrograph was used for this work, and the $K\alpha_1$ and $K\alpha_2$ (1932.30 and 1936.51) lines of iron reflected in the second order from calcite were used as reference lines from which to determine the wave-length of the edges. The dispersion at this position was 20.11X.U. per mm, the crystal-plate distance being 124.4 mm. It was necessary to roll all of the specimens used to a thickness of 0.001 mm in order to secure very distinct edges, and to bring out their character. With absorbing screens of this thickness, the most dense part of the absorption was confined to a narrow band, thus giving the appearance of a white line adjacent to the main edge. Exposures were of the order of 100 ma. hours.

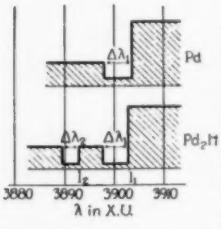

Fig. 2. Diagram of the L_{III} absorption spectra of Pd and of Pd in Pd_2H.

The results of these experiments are shown in Table I, and by the diagram Fig. 2. It is seen that the wave-length of the main L_{III} absorption edge (l_1 in the table) is shifted in the 4.017 phase by 0.87 X.U. (0.6 volts) toward shorter wave-lengths, and that there is in addition a second absorption edge, l_2, which is 10. X.U. (8.0 volts) less in wave-length than the pure Pd edge. The l_1 edge was measured on a comparator reading to 0.001 mm, but the l_2 edge was not dense enough to be measured on the comparator, and the accuracy of these measurements corresponds to about 0.6 volts. The absorption edges of electrolytically charged specimens and of specimens charged from the gas phase were identical in appearance. Microphotograms of the edges are shown in a preliminary report.[9]

Table I. *L_{III} x-ray absorption limits.*

Screen	a_0	l_1	l_2	$\Delta\lambda_1$(volts)	$\Delta\lambda_2$(volts)	l_2-l_1 (volts)
Pd	3.885	3903.90		4.4		
Pd_2H	4.017	3903.03	3893.9	3.8	2.4	7.4

VII. Stability of the Pd-H System

Since the hydrogen-rich phases from the electrolyte and from the hydrogen gas furnace are identical in their lattice constants of 4.017, and also in the character of their L_{III} absorption edges, it seemed probable that the difference in stability might be due to physical causes rather than to an inherent difference in the phases. This is also suggested by the fact that there is only a general agreement among the more than thirty specimens

[9] J. D. Hanawalt, Proc. Nat. Acad. Sci., Dec. 1928.

studied in the length of time necessary for the dissociation or break-down of the 4.017 phase at 20°C in air. After the usual conditions of occlusion, the specimens from the hydrogen furnace were found to go completely from the 4.017 phase to the 3.885 phase in some cases in as short a time as ten hours, and in others as long as six days. The specimens from the electrolyte on the other hand after the usual conditions of electrolysis (one hour at 0.1 to 0.4 ampere per sq. cm), were apparently stable at 20°C in air, though in a month or forty-five days a small part might be found to have dropped to 3.885. About ten days at 70°C is usually sufficient for complete dissociation of the whole specimen, and a temperature of about 200°C is necessary to drive the hydrogen out in a few hours.

The possibility that a sulphide of palladium or any other chemical compound was forming a protecting layer on the surface of the specimens from the electrolyte seems precluded by the fact that electrolysis in H_2SO_4, HCl, and NaOH all gave the same results.

Most of the specimens used were thin sheets of palladium which had been cold-rolled, and in many of them there were evidences of orientation of the micro-crystals as indicated by the extra intensity of some of the diffracted lines on the photographic film. Following this lead, the following experiments were performed. One sheet of palladium which showed orientation was divided into five pieces, two were put into the hydrogen furnace and three into the electrolyte. The two from the furnace showed the same orientation still strongly marked in the expanded lattice, while in the three from the electrolyte, no indication of orientation remained. Those from the electrolyte were stable as usual, while the two from the hydrogen furnace dissociated in four days at 20°C. Further experiments with specimens cold-rolled to 0.001 mm indicated that the instability of the specimens from the hydrogen furnace increased with the amount of cold-rolling. Evidences of orientation were not always present in these cold-rolled specimens, but the instability was just as decided whether the orientation existed or not. If these thin sheets were put in the electrolyte, the 4.017 phase appeared stable as usual. Apparently the process of occluding hydrogen from the electrolyte differs from that of the hydrogen furnace in that the micro-crystals are broken up and the mechanical strains induced by the rolling process are relieved. If mechanical strains are introduced into an electrolytic specimen, it proves to be as unstable as specimens from the hydrogen furnace. Hydrogen was put into a specimen by electrolysis, and it was then cold-rolled from .01 mm down to .003 mm. Immediately after the rolling process, the 4.017 phase still existed alone showing that the hydrogen was not forced out in the process of rolling. Two days later there was a good percentage of the 3.885 phase present, and in eight days the 4.017 phase had completely disappeared, and only the 3.885 phase was present. The control piece which was not rolled, showed no signs of dissociation of the 4.017 phase at the end of thirteen days.

The breaking up of the micro-crystals was observable directly in the x-ray diffraction patterns. By heating the palladium to 1000°C for various

intervals of time, micro-crystals of various sizes could be grown, and three distinct sizes of micro-crystals could easily be distinguished by the appearance of the x-ray picture. Large enough crystals cause separate individual spots on the film, somewhat smaller crystals will give a line, but will be large enough to resolve the Cu $K\alpha$ doublet, while still smaller crystals will not resolve the α doublet. By observing these indications of crystal size, it was seen that the micro-crystals were broken up when the hydrogen was absorbed, but to a greater extent by electrolytic charging than by charging from the gas phase. This difference is probably due to two factors: first, the more rapid occlusion from the electrolyte causing differential strain, and second, the fact that the initial a_0 of the electrolytically charged specimens is considerably in excess of 4.017Å while the a_0 produced in the furnace is always just 4.017Å or only slightly greater. The mechanical strain in the electrolytically charged specimens is diminished to some extent when the hydrogen in excess of the 4.017 phase has escaped. This view is further borne out by the fact that if the electrolytic charging is done with a current density of 0.0001 amp./sq. cm instead of 0.1 amp./sq. cm, so that the initial a_0 does not exceed 4.017, then the specimen exhibits the same degree of instability as the specimens charged from the gas phase.

VIII. Effect on the Pd-H System of Impurities in the Pd

In the early part of the investigation, two specimens of palladium were used whose origin is unknown. They had evidently been used for work in the laboratory some years previously. The behavior of these two specimens as concerns their absorption of hydrogen was distinctly different from the behavior of all of the specimens of pure palladium (99.66% pure) obtained from the American Platinum Co. It was not found possible either by annealing or mechanical working, or removal of the surface layer, to influence the behavior of these two specimens in any way, so an analysis of the material was made. A spectroscopic analysis of one (A) of the specimens of pure palladium and one (B) of the specimens of unknown origin was carried out by Baker & Co., Inc., of Newark, N.J. This analysis showed that the specimen B was distinctly inferior in purity to specimen A. Specimen A was found to contain the usual small amounts of impurities; namely, calcium, magnesium, platinum, copper, iron and silicon. Specimen B contained the usual small amounts of calcium and magnesium, but *considerably* more than usual of copper, iron and silicon. The percentage excess of copper iron and silicon in specimen B above that in specimen A is not known.

The behavior of this, what we may call 'impure' palladium, stands in sharp contrast to that of the pure palladium as described in the preceding pages. Instead of observing the definite distension $a_0=4.017$Å or somewhat larger but no values of a_0 in the range between 4.017 and about 3.885, it was found that the impure palladium specimens could have apparently *any* distension within the region $a_0=3.885$ up to above 4.017, and that there was no stable distension which was characteristic of the system.

When fresh from the electrolyte, this impure palladium had distensions varying, in the nine separate experiments carried out, from $a_0=3.950$ to as

high as $a_0 = 4.030$. Also different distensions existed in different parts of the same specimen at the same time. The following description of one experiment brings out the essential points shown by all of them. The specimen was 3 cm long, 1 cm wide and 0.007 cm thick. It was so supported in the electrolyte that about 1 cm of the length was below the surface. After one hour at 1.5 amp., the distensions ranged from $a_0 = 4.030$ at the lower end to $a_0 = 4.000$ at one cm from the end. Measurements taken at intervals throughout a period of 106 days showed that at all points there was a *continuous* shrinkage to smaller values of a_0 down to 3.888. Raising the temperature simply increased the rate at which the shrinkage took place.

The effect of mechanical strain on these impure palladium specimens was the same as that on the pure palladium; namely, to increase the rapidity of the dissociation of the Pd-H system. A specimen was cold-rolled from 0.07 mm to 0.001 mm; after the rolling it still contained hydrogen, a_0 being 3.940. A picture taken eight hours later contained broad diffraction lines, showing that micro-crystals with a_0 from 3.930 to 3.885 existed close together. This may be due to the more rapid dissociation of the micro-crystals with the greater strain. Three days later the specimen had completely dropped to 3.885, while the part of the specimen which was not rolled showed no detectable dissociation in three days.

IX. Discussion of Experimental Results

The results of this study indicate that in the range between $a_0 = 3.885$Å and 4.045A there exists just one outstanding stable lattice parameter of the Pd-H system; namely 4.017Å, regardless of the method used to occlude the hydrogen. And since pressure-concentration equilibrium studies show 'breaks' only at the concentration 0.5, it seems certain that the value 4.017 corresponds to the composition Pd_2H. The source of the discrepancy between this work and that of Linde and Borelius is not clear. As has been stated in the introduction to this paper, Linde and Borelius find different distensions of the Pd lattice depending on the method of occluding the hydrogen. The absorption of hydrogen from the gas phase, in the present work, was carried on under the conditions described by them so that their value 3.978 should have been observed. On the other hand, the phase 4.017 occurred every time the experiment was performed by us, and should have been observed by them. There is a possibility that the difficulty lies in the fact that Linde and Borelius used a different x-ray spectrograph for their electrolytically charged specimens than for their hydrogen furnace specimens, and that the latter had a film radius of only 2.5 cm.

It is well known that x-ray absorption limits of elements are changed by the valency or state of chemical combination of the element, and that in chemical compounds in addition to the principal edge, there may also be secondary edges or 'fine structure.' On this basis the results of the x-ray absorption work on the Pd-H systems indicate that the hydrogen is in chemical combination with the palladium. There seem to be at least two possible interpretations of the complex absorption edge exhibited by Pd_2H.

Since there are twice as many Pd atoms as H atoms present, the complex edge might correspond to a Pd atom which shares an H atom with one other Pd atom, or secondly, it might correspond to the superposition of two simple edges, one, l_1 due to Pd atoms alone, and the other, l_2, due to Pd atoms with which are combined H atoms. If we accept the first point of view, then it should be remarked that it seems unusual to find fine structure caused by chemical combination, and yet the main edge remaining almost unchanged as it is in this case. If, on the other hand, we accept the second hypothesis, then we have the result that combination with the hydrogen atom causes the L_{III} absorption limit of the Pd atom to shift 10. X.U. toward shorter wave-lengths, and that the L_{III} limit of the remaining Pd atoms which are not in intimate association with H atoms has been shifted by 0.87 X.U., perhaps due to the effect of the greater isolation of the atoms in the expanded lattice.

On this basis the crystal lattice of Pd_2H would be a face-centered cubic lattice in which alternate grating points are occupied by Pd atoms. Then higher concentrations of hydrogen than 0.5, (Pd_2H), would correspond to more of the grating points being occupied by PdH molecules than by Pd atoms. Whereas, if the hydrogen atoms in Pd_2H were shared between two palladium atoms, then for concentrations higher than 0.5 the excess hydrogen atoms would have to be associated in some different manner. The recent results of Coehn[7] showing that at least some of the hydrogen is in the ionic state may be of importance in this connection.

That the Pd-H system is composed of the units Pd and PdH has been suggested by Linde and Borelius on the basis of experiments on the behavior of the electrical resistance. Oxley[8] has also suggested on the basis of susceptibility measurements that the hydrogen is in intimate association with the palladium.

Since the effect of impurities in the palladium was to give results identical with those of Yamada, while the results with pure palladium agreed with McKeehan's work, this would seem to be the source of the difference in their results. Yamada's interpretation of his results to mean a solid solution of hydrogen in palladium, and not a chemical combination is not a necessary one since his results may also be explained on the assumption that the hydrogen atom is combined with a palladium atom, but that the symmetrical and stable arrangement Pd_2H with $a_0=4.017$ cannot be attained because of the presence of foreign atoms (which do not combine with hydrogen atoms) in place of palladium atoms at some of the grating points.

The fact that the distensions in the range between $a_0=3.885$ and 3.920 in the sputtered Pd specimens remained unchanged over a period of two years at 20°C might be explained on the assumption that these specimens were free from mechanical strain. The process of 'building up' the material in the presence of atomic hydrogen being different in this respect from the

[7] Coehn, Naturwissenschaften **11**, 183 (1928).
[8] Oxley, Roy. Soc. Proc. **A101**, 264 (1922)

process of occluding hydrogen in palladium which is already in the crystalline state.

X. Summary and Conclusions

1. X-ray investigation of the crystal lattice of the Pd-H system showed that after electrolyzing in dilute H_2SO_4 specimens might have various distensions with a_0 in the range 4.017 to 4.045, but that in the course of ten days or less at 20°C those with a_0 greater than 4.017 would shrink down to this value, but not below it.

2. This value 4.017 is independent of the temperature at which the specimen is held in a range up to about 80°C. If the temperature is raised higher than this, the phase with $a_0=4.017$ dissociates completely, and a_0 becomes 3.885, (pure palladium).

3. Palladium which absorbs hydrogen from the gas phase shows the identical value $a_0=4.017$ and behaves in the same way as the electrolytically charged specimens. The difference reported by Linde and Borelius was not observed in this work.

4. A greater stability of this 4.017 phase in some electrolytically charged specimens as compared with the specimens from the hydrogen furnace is associated with a difference in the mechanical state of the micro-crystals in the two cases.

5. The existence of the unique value $a_0=4.017$ and the results of other observers on the pressure-concentration equilibrium of the Pd-H system lead to the association of the lattice parameter 4.017 with the concentration Pd_2H.

6. X-ray absorption pictures of the L_{III} limit of palladium show that the presence of the hydrogen causes a shift of the main edge of 0.87 X.U. toward shorter wave-lengths, and the occurrence of a secondary absorption 10 X.U. toward shorter wave-lengths. This is taken to mean that the hydrogen is in chemical combination with the palladium. The appearance of the edge may be explained on the hypothesis that it is the superposition of two absorption edges, one due to the molecule PdH and the other due to the atom Pd.

7. A study of palladium containing certain impurities showed that *any* value of a_0 between 3.885 and 4.017 was possible, and that these phases showed a continuous shrinkage with time to smaller values of a_0. This agrees with Yamada's work on palladium, while the results with pure palladium correspond with those of McKeehan, indicating that the source of the discrepancy between those two investigations may be impurities in the palladium.

In conclusion, the writer wishes to express his appreciation to Dr. C. E. Mendenhall for many valuable suggestions, and to Dr. L. R. Ingersoll for his kindness in making the sputtered Pd specimens.

University of Wisconsin.
November 22, 1928.

THE EVAPORATION OF THORIUM FROM TUNGSTEN

By Mary R. Andrews

Abstract

The rate of evaporation of thorium from pure tungsten and from carbonized tungsten was measured between 2000° and 2500°K. The thorium was deposited on these surfaces by evaporation either from thoriated filaments or from metallic thorium. Evaporation from both surfaces was found to vary directly with the fraction covered, being more rapid from pure tungsten than from carbonized tungsten. Heat of evaporation from tungsten was calculated to be 177000 cal/gr-atom and from carbide 202000 cal.

THE evaporation of thorium from a tungsten surface has been determined by Langmuir[1] by measuring the rate of loss of electron emission power of a filament containing thorium; but such a measurement is complicated by the diffusion of thorium to the surface from the interior of the filament so that the change in electron emission depends on two factors: (1) the loss of thorium from the surface by evaporation, and (2) the replacement of the thorium on the surface by diffusion from within the filament.

It was thought, therefore, worth while to make a few experiments in which thorium deposited from external sources on pure tungsten was allowed to evaporate. The experiments were performed with tubes which contained four filaments. The two middle ones were hairpins of four mil pure tungsten wire ten centimeters long. In most of the experiments the two outer filaments were of 8.5 mil tungsten containing two percent of thoria. In a few, however, tungsten coils surrounding short rods of metallic thorium were used. Filaments were spaced about a centimeter apart. After degassing, one of the middle filaments was carbonized by running it at incandescence in a very low pressure of naphthalene vapor.

Great precautions were taken to produce a good vacuum. The filaments were welded to heavy molybdenum leads and thoroughly degassed. The anode was a calcium mirror deposited on the walls of the tube from a piece of wire heated by a tungsten spiral in the lower end of the tube, and connected to the main tube was a side tube containing degassed absorbent charcoal which was immersed in liquid air during the experiments.

It was found very difficult to maintain emission at temperatures at which evaporation of thorium was negligible, with voltage on the anode, when the tube was connected to the pumping system or was trapped off by a mercury trap and liquid air trap. The following data, therefore, were obtained after the tubes were sealed off the exhaust system. The persistence of emission at temperatures below 2000°K was used as a test of good vacuum in these tubes. If not successful at first, it was usually so after the second deposition of thorium, the evaporation and redeposition of thorium and

[1] Langmuir, Phys. Rev. **22**, 357 (1923).

tungsten being an excellent way to clean up residual gas. The effect of gas was much more marked on the uncarbonized than on the carbonized filaments.

Temperatures of uncarbonized filaments were controlled by their watts input. These were calculated from Forsythe's and Worthing's[2] data for watts/cm². Correction for cooling of the ends was made according to the cooling curve published by Dushman and Ewald[3] except that twice the published value for ΔV was used, this value having been found by the authors to have been determined for one lead only. The carbonized filaments were run at twenty percent greater energy input than calculated for an uncarbonized filament. This factor (1.2) is an average of a number of photometric determinations made by the author some years ago. Carbonized filaments vary considerably in their emissivity depending on the state of the carbonized surface, so that there is a probability of some error in the case of any particular filament. The carbonized filaments in these experiments were prepared under as nearly the same conditions as possible, but the irregularity in the results may be laid to these unavoidable inaccuracies in temperature.

It was found necessary to run the two thoriated wires for an hour or more at 2800°K in order to cover the surface of the middle filaments completely enough (eight-tenths or more) to give a satisfactory emission. After such a deposition, when the emission from either of the middle (coated) wires was studied, it was found to increase at first quite rapidly at any constant filament temperature between 1800° and 2200°. It is assumed that this activation is due to the fact that some tungsten is evaporated from the thoriated filaments, and deposits on the test filaments along with the thorium. During the first few minutes of heating such a filament, therefore, the deposited atoms become rearranged, the thorium diffusing outward to form a more or less complete surface layer, and undoubtedly also diffusing to a slight extent down into the tungsten. This diffusion inward might be a disturbing factor in that later, during the evaporation of the surface layer, it would be possible that some thorium might again come to the surface and replace that which has evaporated. Since, however, an extremely thin layer (probably not over ten atoms thick) was deposited and since all the thorium atoms coming to the surface under other thorium atoms would immediately cause the evaporation of these atoms, it is easily seen that the diffusion of thorium atoms would be almost completely toward the surface and that the layer deposited would be very quickly exhausted of thorium, leaving only a monatomic adsorbed layer on the surface.[4]

The procedure followed in determining the rates of evaporation, therefore, was (1) deposition of thorium and tungsten from the thoriated filaments or from the metallic thorium on the pure tungsten filament and carbonized filament, (2) running one of the coated filaments at, say, 2000°, until activation had reached a maximum, (3) running this filament at a known tempera-

[2] Worthing, Astrophys. J. **61**, 129 (1925).

[3] Dushman and Ewald, G. E. Review **26**, 154 (1923).

[4] For the mechanism of the formation of a thorium covered surface see Langmuir, reference 1.

ture and measuring the decline in emission with time. Emission measurements were made at 1500°K. After both filaments had been so tested, they were

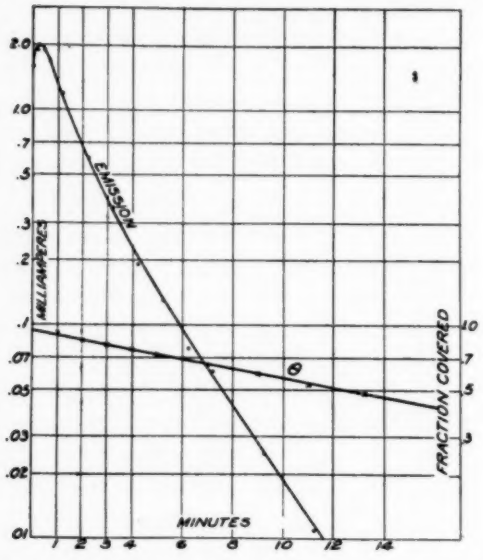

Fig. 1. Evaporation of thorium from carbonized tungsten at 2400°K.

run at a somewhat higher temperature (the carbonized filament not over 2500°) until the emission had fallen to the value for pure tungsten, the deposition of thorium was again made, etc.

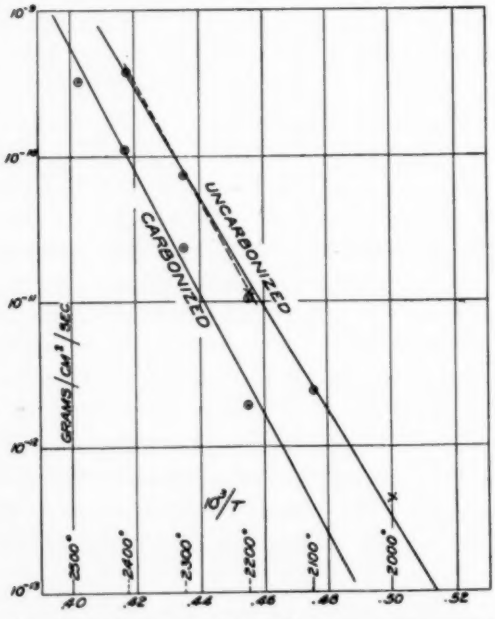

Fig. 2. Rate of evaporation of thorium vs. temperature.

Fig. 1 shows a characteristic evaporation curve. In this case it is obvious that the preliminary activation had not been quite complete.

At 1500° the emission from this filament if completely covered with thorium should be 4.00 milliamperes.[5] From the pure tungsten surface the emission at 1500° is 0.018 microamperes.[6] From these data, and the above evaporation curve, the fraction of the surface covered (θ) at any instant is easily calculated.[1]

The straight line in Fig. 1 marked θ shows that the surface of thorium decreases logarithmically with time. The slope of this line $d \log \theta/dt$ gives the rate of evaporation or the fraction of the surface covered which evaporates in one second.

Table I gives in column two values of $d \log \theta/dt$ for carbonized and uncarbonized filaments at various temperatures. Assuming that there are 0.756×10^{15} atoms of thorium per square centimeter, the grams of thorium and the number of atoms evaporated per second from a completely covered surface can be calculated. These values are given in columns 3 and 4 and the former shown in Fig. 2. It is of interest to note that they are not very different from the values for the evaporation of tungsten as given by Jones, Langmuir and Mackay.[7] They report 1.25×10^{-11} grams/cm² at 2200° and 4.36×10^{-10} at 2400°. The tungsten data are shown on Fig. 2 by the dotted line.

TABLE I. *Evaporation of thorium at various temperatures.*

Temperature	$\frac{d \log \theta}{dt}$	Evaporation grams/cm² sec.	Evaporation atoms/cm² sec.
	Uncarbonized filaments		
2100°K	8.4×10^{-6}	2.45×10^{-12}	6.35×10^{9}
2200	3.7×10^{-5}	1.08×10^{-11}	2.8×10^{10}
2300	2.5×10^{-4}	7.29×10^{-11}	1.9×10^{11}
2400	1.3×10^{-3}	3.79×10^{-10}	$.98\times10^{12}$
*2000	1.5×10^{-6}	4.4×10^{-13}	1.1×10^{9}
*2200	4.0×10^{-5}	1.17×10^{-11}	3.0×10^{10}
	Carbonized filaments		
2200°K	6.6×10^{-6}	1.92×10^{-12}	5.0×10^{9}
2300	8.5×10^{-5}	2.38×10^{-11}	6.4×10^{10}
2400	3.8×10^{-4}	1.11×10^{-10}	2.9×10^{11}
2485	1.14×10^{-3}	3.32×10^{-10}	$.86\times10^{12}$

* Thorium deposited from metallic thorium

From the above values, using the Clapeyron-Clausius equation in the form

$$Q = 2.303\ R[d \log P/d(1/T)]$$

the heat of evaporation of thorium can be calculated. For evaporation from pure tungsten $Q = 177000$ calories per gram atom, from carbonized tungsten it is 202000 calories. Langmuir's value for evaporation of thorium from tungsten is 204000 calories. For evaporation/cm² his figures are three to nine times those of the author.

[5] Dushman and Ewald, Phys. Rev. **29**, 857 (1927).
[6] Dushman, Rowe, Ewald and Kidner, Phys. Rev. **25**, 338 (1925).
[7] Jones, Langmuir and Mackay, Phys. Rev. **30**, 201 (1927).

The results given above differ from those of Langmuir[1] in one essential. He found that the rate of evaporation of thorium at constant temperature was constant independent of the fraction of the surface covered except where this fraction was very small. This was considered to be due to the attraction of the thorium atoms for each other, so that when the surface was almost completely covered and the thorium atoms were in contact with each other, they tended to hold one another in place. Hence the fraction of thorium atoms evaporating increased as the surface became less completely covered. The author's data show a rate of evaporation which is a linear function of the surface covered, i.e., a constant fraction of the amount of thorium on the surface, indicating that the attraction between the thorium atoms is negligible at the temperatures used.

In conclusion the author wishes to thank Dr. Langmuir, Dr. Saul Dushman and Mr. Heinz Specht for their interest and help in this work.

RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY,
SCHENECTADY, NEW YORK,
November 23, 1928.

BOOK REVIEWS

Thermionic Phenomena. EUGENE BLOCH, translated from the French by J. R. CLARKE. Pp. 145, 24 figs. E. P. Dutton and Company, New York, 1928. Price $2.50.

Thermionic phenomena are becoming increasingly important as physicists turn their attention to the new theories concerning electrons in metals and the actions taking place at the surfaces of metals. An up-to-date (1928) compilation of the numerous experimental results and theories would be very welcome. This book is a translation of one of the "Conférences-Rapports." It gives an introduction to the subject and its literature up to the date of the French edition (1923). As stated by the author, Richardson's book (1921) is drawn upon to a large extent. A chapter on the applications of thermionic phenomena to the measurement of high vacua and the rectification of alternating currents is included. The English translation has a subject and author index.

J. W. BUCHTA

Practical Television. E. T. LARNER. Pp. 175, 97 figs. D. Van Nostrand Company, 1928. Price $3.75.

This is an elementary presentation of the principles underlying television and the transmission of pictures over telephone lines and by radio. Brief descriptions are given of a large number of the earlier attempts to produce a successful television apparatus, thus showing how the present arrangements were evolved. There are chapters on selenium and the selenium cell, photoelectricity and the photoelectric cell, images and their formation, and cathode rays, giving elementary discussions of these subjects.

The book emphasizes the European developments which are not so well known to the American public as those of the American Telephone & Telegraph Company.

J. W. BUCHTA

The Theory of Light. THOMAS PRESTON, edited by A. W. PORTER. Pp. 643+xxiv, 248 figs. Macmillan and Company, New York, 1928. Price $8.00.

One of the pioneer English textbooks on the wave theory of light was Preston's "Theory of Light." The present fifth edition edited by A. W. Porter still holds its place as one of the more comprehensive general texts on the classical theory of light. The older editions of this book are sufficiently well known to physicists that a comparison of this edition with the previous ones will suffice.

The general outline is the same as that of the fourth edition; in fact, most of the paragraphs are identical. In the first six chapters, a short paragraph on intrinsic brilliancy, problems on thick lenses and about ten pages on the aberration of lenses are the chief additions. In later chapters we find additions or change in the following topics;—influence of pressure on refractivity of gases, color of thin plates, Michelson's measurements on stellar diameters and recent measurements on the velocity of light, the echelon spectroscope, Lummer-Gehrcke interferometer, and the resolving power of instruments. The chapter on diffraction has been rearranged to separate the description of the Fresnel and Fraunhofer diffraction phenomena. The treatments of Fresnel integrals and MacCullugh's theory have been shortened. Other minor changes also occur. The brackets separating the additions to the original text by later edition have been removed.

No attempt is made to discuss the modern theories of radiation. Planck's "h" does not appear in the book.

A new index is supplied which is shorter, having fewer double entries.

J. W. BUCHTA

Solubilities of Inorganic and Organic Compounds, Volume II. ATHERTON SEIDELL. D. Van Nostrand Company, New York, 1928. Pp. vi+569. Price $8.00.

This supplement has the same format as the first volume of the second edition. Its pagination is consecutive with the latter. It contains data published from 1917 to 1926 on the solubilities of inorganic and organic compounds. The necessity of adding 569 pages in making this supplement shows how rapidly publications on solubility have increased during the last decade.

The same thoroughness has been exercised in the preparation of this volume as in the previous one. The Author's regret that a third edition in a single book rather than the issuance of a supplement was not possible because of cost should, the reviewer believes, cause him no worry as the present two volumes are very satisfactory.

M. C. SNEED

Handbuch der biologischen Arbeitsmethoden Teil A Heft 6 Elektronen-und Ionenröhren. FERDINAND SCHEMINZKY. Pp. 442, 239 figs. Urban and Schwarzenberg, Wien, 1928 Price RM 25.

The book is written for biologists with the purpose of describing methods employing electron and ion tubes. It is a part of a handbook on biological methods and it is written in a popular fashion in eight chapters, as follows: 1. Construction and action of electron tubes. 2. Applications of the electron tube. 3. Multi-stage amplifiers. 4. Special applications of the amplifier. 5. Auxiliary apparatus. 6. Measurements. 7. On the construction of tube circuits. 8. Sources of errors and disturbances.

Much space is given to the action of the electron tube as well as to its construction. The applications in Chapter 2 give an idea how the tube acts as a resistance, as a rectifier, as a d.c. and a.c. amplifier, as an oscillator, and as a measuring instrument. Chapter 3 describes in detail transformer-coupled, resistance-coupled, and resistance-capacity-coupled amplifiers as well as the amplification of high frequency currents. Chapter 4 deals with amplification of bioelectric currents, of sound waves and amplification of light intensities, while Chapter 5 describes in detail telephone receivers, loud speakers, exponential and conical horns, relay circuits, and the action of resistance, capacity and inductance.

Generally speaking, the physical concepts of the book are brought out very clearly, but it seems strange that so much space in a book that should give information to a man working in the biological field should be given to measurements of amplification factor or to detailed description of tube sockets, design of exponential and conical horns, tube oscillations of the second type, etc.

The well-known circuits for d.c. amplification and the amplification of bioelectric currents are no doubt of great interest to the worker in the field and the precautions to be taken for such work are brought out very well.

AUGUST HUND

Gruppentheorie und Quantenmechanik. HERMANN WEYL. Pp. 281. S. Hirzel, Leipzig, 1928. Price, RM 20.

This book gives a mathematically elegant presentation of quantum mechanics. The characteristic features of Weyl's point of view have been summarized by him in the Zeitschrift für Physik **46**, 1927, page 1. The book gives a detailed treatment along the same lines. The mathematical concepts necessary for the statement of the physical postulates are formulated in the first chapter. Unitary geometery and hermitean forms are introduced here. The second chapter starts out with pointing out reasons for having a quantum theory: Planck, Einstein, Bohr. Then wave-mechanics is introduced. A consideration of phenomena of collisions leads up inductively to a formulation of quantum mechanics by means of matrices. This chapter also includes discussions of Heisenberg's uncertainty relation (in a very simple way following a suggestion of Pauli), the theory of perturbations, canonical transformations of variables, the Schroedinger-Gordon relativistic equation. The chapter is concluded with a derivation of Einstein's transition probabilities by Dirac's method of quantizing amplitudes. This physical section is followed by the mathematical chapter III in which the fundamental

notions of group theory are presented and illustrated by means of four examples which prove of great value in physical applications discussed in chapter IV. At this point the important part of the book begins. It includes discussions of angular momentum, inner quantum numbers, selection and intensity rules, electron spin (Pauli's matrices) multiplet structure and anomalous Zeeman effect as subheads under the group of rotations; the Lorentz group gives Dirac's wave equation; Heisenberg's resonance phenomenon, Pauli's exclusion principle, the periodic table, the quantization of the wave equation (Jordan and Klein and Jordan and Wigner) and the application of Abelian groups to kinematics are also treated.

The quantization of the wave equation is carried out in many respects more lucidly than in the papers referred to.

The last chapter V is devoted to a study of the permutation group with discussions of noncombining term systems (Wigner, Hund) and chemical combination along the lines of London and Heitler.

The importance of the book is a sufficiently detailed discussion of the connection between quantum mechanics and a well-worked-out branch of mathematics. This makes it possible to present the subject more elegantly than has been done without groups. The treatment although logical and clear is not always easy to follow. References to definitions of symbols introduced in previous chapters are not always available. Thus on page 152 of chapter IV D_j is that introduced on page 107 chapter III, the definition $\overline{A}=\overline{A}^*$ on page 16 could have been written in a separate line. It would be helpful to have a list of symbols with references to the places where they are defined and where their most important properties are treated

G. BREIT

Vorlesungen über Nichteuklidische Geometrie. FELIX KLEIN. Die Grundlehren der Mathematischen Wissenschaften, Band XXVI. Pp. 326+XII. Julius Springer, Berlin, 1928. Price, RM 19.50.

Non-Riemannian Geometry. L. P. EISENHART. American Mathematical Society Colloquium Publications, Volume VIII. New York, 1928. Pp. 184+VIII.

Non-Euclidean Geometry is important for a Physicist mainly because it was the first step in the development which in the 19th century again made Geometry an experimental science—in a certain sense part of Physics—and so prepared ground for the further development which led to the attempt to make Physics part of Mathematics—the General Relativity Theory. This aspect of non-Euclidean Geometry which connects it with Differential Geometry, as well as the history of the subject are discussed in Klein's book—which appears now for the first time in printed form—in a most illuminating way but this discussion occupies a comparatively small portion of the book. The basis of the exposition forms the approach to non-Euclidean Geometry through projective Geometry. This latter is not assumed to be known but is developed from the beginning in a masterful and thorough fashion in Part I (127pp.) which constitutes an excellent text book in Projective Geometry. On that basis Klein who introduced. this approach half a century ago builds non-Euclidean Geometry in part II (about 140 pages). The third part (not quite 50 pages) deals with relations of non-Euclidean Geometry to other subjects including the aspects mentioned in the beginning.

If non-Euclidean Geometry may be considered as the first step in the development which led to General Relativity non-Riemannian Geometry appears as an outgrowth of it, as a by-product. It seemed that the Geometry established by Riemann as a generalization of the theory of surfaces which was adapted admirably to take account of gravitation was not general enough to include electromagnetism and several other geometries obtained by dropping what seemed to be a fundamental feature in Riemann's Geometry—the metric were proposed to remedy this situation. The most recent of such attempts, Einstein's *New Theory*, makes use of non-symmetric displacements (asymmetric connections) which are treated in the first Chapter of Eisenhart's book. The situation as far as Physics is concerned is not quite clear at present; but for Mathematics the result was a beautiful new theory. The book written by one who took part in creating the theory gives a very complete account of literature up to the beginning of 1928. The exposition leaves nothing to be desired.

G. Y. RAINICH

Introduction to Theoretical Physics. LEIGH PAGE. Pp. 587+x, 201 figs. D. Van Nostrand Company, New York, 1928. Price $6.50.

This book is a noteworthy contribution to American literature in physics. It fills adequately the lamentable hiatus which has existed between our text books in general college physics and advanced treatises on more specialized subjects. Those of us who for years have attempted by courses of lectures to bridge over this gap in a systematic unified way welcome this book as the first adequate text book of its kind which has been written for the American student.

The subject matter is divided into five main divisions. Dynamics, hydrodynamics, thermodynamics and the kinetic theory of gases, electromagnetism and optics and spectroscopy. The introduction (39 pages) presents the elements of the vector analysis which is systematically used throughout the book in the mathematical formulation of the subject matter. The only mathematics required of the reader in advance is a good working knowledge of the differential and integral calculus and an acquaintance with the elements of differential equations.

The book is profusely illustrated and numerous problems have been interspersed through the text.

The style is lucid and the treatment in the main logical and clean-cut. In the section on mechanics one might quarrel with the casual introduction of mass, without definition or discussion of its significance, but in this the author has at least the preponderance of precedent in his favor.

The printing and binding are attractive and serviceable.

JOHN T. TATE